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MINERALOGY AND GEOCHEMISTRY OF PARENT MATERIALS OF THE ATHABASCA TAR SANDS REGION

by

GRAEME A. SPIERS

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH

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IN

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Supervisor

J.W. Increnek

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I. Ed W. May

Date 29 April, 1982

DEDICATION

TO ALLIE AND TRIXIE

TO MARIE, RACHEL AND JUDE.

ABSTRACT

This investigation of the mineralogical and geochemical variation of parent materials from North East Alberta was undertaken to provide baseline information on the levels of 18 major and minor elements within the Athabasca Tar Sands Region. Levels of 16 elements (Al, Cr, Cu, Fe, K, Mn, Mo, Na, Ni, P, Pb, Sr, Ti, V and Zn) tended to be highest in the north west of the region, and lowest in the north east. Numerical analysis and elemental contour maps indicated that the variabilty of these elements was related to the variability in clay content of the parent materials. Levels of Ca and Mg were highest in the calcareous lacustrine and morainal materials in the west-central sector of the region.

Regression equations were calculated, in which minor element levels were the dependent variables and major element levels were the independent, to determine whether macroelement levels could be utilised to predict minor element abundance. The most important "predictor" elements were Al, Fe and K; these explained between 45 % and 90 % of the minor element variance. This suggests that minor element variability was related to variation in clay mineral species. Pb was the exception, with over 90 % of the explained variance of the regression equation being related to Ti,suggesting that much of the Pb variability in these parent materials may be related to occlusion in the weathering products of both Ti and Fe.

Factor analysis indicated a high degree of interrelationship among individual trace element levels which in turn were linked with Fe, Al and Ti levels. This association described 70 % of the chemical compositional variance of the parent materials. This variance was related to the variability in ionic substitution in the octahedral and tetrahedral layers of clay minerals in the parent matrials. Another 15 % of the variability was ascribed to Ca and Mg and thus to pH of the parent materials. The remaining variance was explained by Mn (8 %) and Sr (6 %). The former (Mn) was related to the presence of manganese nodules and mangans, and the latter (Sr) to mica variability. Subsequent factor analysis of minor and major elements as separate groups further defined the above general relationships, with variability in micaceous and smectite mineral structural composition being implicated as factors explaining the regional bulk chemistry variation.

Characterisation of clay separates from the four major Soil Units of the region indicated that all were dominated by micaceous minerals, smectites, kaolinite and chlorite.

Isotopic analyses (^{18}O) of the clay separates indicated that the levels (13.5 $^{o}/_{oo}$) from the Kinosis Unit, to the east of the region, were similar to those documented for clay minerals in the Athabasca Group metasediments. The levels (16 - 17 $^{o}/_{oo}$) for the Legend Unit, in the north west, are the same as those for marine Cretaceous sediments, which comprise a large component of the matrix of the parent material of this Unit. Detailed examination of the individual clay species found in these two Units indicated that the Legend Unit had a significant component of non-ideal beidellite, whereas that in the Kinosis Unit was ideal in structure. The micaceous and montmorillonite species in these units display no significant differences, and the kaolinites are b-axis disordered in both. Dickite is present in the coarse clay separate of the Kinosis Unit.

The partitioning of the minor elements among the clay species, based on numerical analysis, demonstrated that B, Cu, Mo, Ni and Zn are probably in the authigenic smectites, and Co, Cr and V are in the micaceous minerals. Mn, Pb and Ti are in the weathering products such as haematite, goethite or X-ray amorphous compounds, whereas Sr appears to substitute randomly for K in the mica structure. This variability of individual elements as structural components of the individual phases of the clay separates was related to the diversity of provenance of the parent materials of the individual Soil Units.

The sand mineralogy displayed marked similarity between all groups, with quartz being the dominant mineral. The contents of Ca-feldspar, K-feldspar and Na-feldspar were similar in all units, as were the levels of individual heavy mineral species.

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This question has often been asked:

"Why come to Edmonton?"

Dr. J. Shaw, late of the Department of Geography, suggested many years ago, whilst being taught how to milk cows in Godzone, that Edmonton, climate and locale aside, is not such a bad place to live and that it may be possible to learn something new here.

He was correct on both counts.

As in any study of this type recognition must be given to many whose names do not occur on the final document. The responsibility for the initiation of this thesis must rest on the shouders of two Kiwis, Professors J.D.McCraw and H.S.Gibbs; the former always emphasised that "the answer lies in the soil" and the latter deserves acknowledgement for the profound statement that "all yellow dirt is not clay."

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1. INTRODUCTION

Between 1976-1978 the field phase of a soils inventory was completed to provide baseline data concerning the kinds, characteristics, locations and extent of soils and landforms in the Alberta Oil Sands Environmental Research Programme (AOSERP) study area. The information provided is to be used as an aid in identifying the nature of the interactions of some of the biotic and abiotic components of the environment; to predict the effect of oil sands development on the environment; to identify materials useful in reclamation procedures; to aid selection of research sites; to provide information for land-use planning and development; and to aid in monitoring changes in resources caused by development (Turchenek and Lindsay, 1981).

The soil survey approach is basically an integrated study of the soil forming factors -climate, parent materials and topography acting over time- to produce a map delineating the areal variation of soil units. It was realised early in the course of this survey that very limited information was available on the chemical and mineralogical nature of the parent materials in this region , although these inherently determine the taxonomic classification of the soil solum. The parent material contributes such basic characteristics to the solum as colour, texture, structure , mineralogic composition and physico-chemical properties.

This research was initiated to obtain comprehensive information on the chemical and mineralogical nature of the parent materials within the study region. The proximity of the area to the boundary between the Precambrian, Paleozoic, and Mesozoic bedrock formations which strike almost perpendicular to the Quaternary ice-flow directions suggested the possiblity of defining clay and sand mineralogical parameters unique to the provenances of the major soil forming sediments of the region.

Samples were collected from parent materials within the AOSERP study area and analysed with the following broad objectives:

1. To determine quantitatively base levels of major and minor elements within these soil parent materials of significant areal extent within the region.
2. To evaluate by Principal Factor Analysis the association of these elements with the textural parameters of the sediments.
3. To determine the clay mineralogy of the Kinosis, Legend and Horse River glacial till

units, and the glaciolacustrine sediments of the Dover and Hangingstone Plains.

4. To assess the relative contribution of different provenances to the local glacial sediments through use of oxygen isotopic analysis of clay separates.
5. To characterise the mineralogy of the sand fraction of the above parent materials.
6. To differentiate surficial geological units using clay fraction and bulk chemistry of the fine earth (<2 mm) fraction.

Numerical taxonomy approaches were used to objectively classify the samples into hierarchical units which were then correlated with units differentiated by routine soil survey procedures. The intent of this approach was to examine the relationship between a quantitative and a qualitative approach to the classification of surficial materials.

2. THE STUDY REGION.

2.1 LOCATION:

The study region consists of Township 84 to 104, in Ranges 6 to 18 West of the Fourth Meridian, and Township 105 to 115, in Ranges 6 to 9, excluding Wood Buffalo National Park, in the Province of Alberta (Figure 1). The total land area is about 305 townships, or 28,440 square kilometres (Turchenek and Lindsay, 1981).

2.1.1 Climate:

The climate of the region is continental with relatively short, cool summers during which temperatures rarely rise over 30° C (Longley and Janz, 1978). About two thirds of the precipitation occurs in the summer months, much of it in the form of major rainstorms. High winds occur infrequently in the area. Topography does not have a major effect on weather patterns, although terrain features such as the Birch Mountains may influence wind patterns. Mean daily temperatures for Fort McMurray, the major population centre of the region, are 16.3° C in July and −21.5° C in January. Annual precipitation is 304.6 mm rainfall and 139.7 mm snowfall. Total precipitation decreases northwards through the region.

Fort McMurray experiences an average of 223 days of frost, with an average frost free period of 69 days. Winter temperatures are slightly higher and summer temperatures slightly cooler in the uplands in comparison to the lowlands and plains of the study area.

2.1.2 Vegetation:

The study area is located in the Boreal Forest Region (Rowe, 1972). The principle tree species are white spruce (*Picea glauca*), black spruce (*Picea mariana*),balsam fir (*Abies balsamea*), jack pine (*Pinus banksiana*), aspen (*Populus tremuloides*), balsam poplar (*Populus balsamifera*), and white birch (*Betula papyrifera*). The four Forest Sections found within the study region are the Mixedwood, Upper MacKenzie, Athabasca and Northwestern Transition sections (Rowe, 1972). The major vegetation types in the study area were examined by Stringer (1976), and fitted within the scheme of Thompson

et al. (1979).

2.1.3 Physiography:

The area lies within two major physiographic provinces– the Interior Plains and the Precambrian Shield (Atlas of Alberta, 1969). The subdivision of the provinces into regions, sections and districts was completed by Pettapiece (1981). Descriptions of these facets of classification may be found in the report by Turchenek and Lindsay (1981).

2.2 BEDROCK GEOLOGY

As glacial tills may contain up to 85 per cent local bedrock materials in their fabric and composition (Bayrock, 1962) the underlying geological formations are of considerable importance (Twardy *et al.*, 1974). The bedrock geology map (Figure 2) was derived from the bedrock geology map of Alberta (Green, 1970).

Precambrian rocks, primarily metasediments, granite gneisses and porphyritic granites, subcrop and outcrop to the northeast of the area. The clay mineralogy of the Athabasca Group (sandstones and conglomerates) consists of kaolinite and illite in varying proportions, with or without chlorite as a significant third component. Smectites are noticeably absent (Hoeve *et al.*, 1981).

Carrigy (1959) described the Devonian rocks of the region as consisting of evaporites (calcite, dolomite, halite, gypsum, anhydrite, and organic carbonates). The clay minerals identified in the various Paleozoic Formations were illite, kaolinite, chlorite. Potassium feldspars were important in insoluble residues of Paleozoic limestones (Carrigy, 1963). The Lower Cretaceous geologic units were found to have two distinct provenances, the Precambrian Shield to the east and the Cordillera to the west (Carrigy, 1959, 1973). The mineral composition of the McMurray Formation is primarily quartz, K–feldspar and muscovite in the sand fraction with associated tourmaline, zircon, chloritoid. Some garnet and kyanite are present in the heavy mineral fraction. The clay fraction is dominated by kaolinite and illite, with an apparent absence of any expandable components.The Clearwater Formation has quartz and small quantities of feldspar in the sand fraction, and montmorillonite, illite, kaolinite and chlorite in the clay fraction.

Many of the feldspar grains in the Mesozoic sediments are relatively unweathered and were K/Ar dated at 1.35 – 1.55 * 10^9 years B.P. (Williams *et al.* (1962) in Carrigy, 1963), thus indicating derivation from a Precambrian source to the northeast. Some of the feldspar grains (Ab80:An20) in the Clearwater Formation have a glassy groundmass indicating volcanic origin. Ross and Hendricks (1945) state that volcanic glass with a crystalline component of feldspar in the presence of Mg ions from seawater alters to form smectites. Smectites are ubiquitous in the Upper Cretaceous rocks of Alberta, and have been suggested as a possible time stratigraphic marker within Lower Cretaceous sediments (Carrigy, 1963).

The Upper Cretaceous rocks of the Alberta Plateau remnants are predominantly marine shales and silty shales (Smokey Group,Dunvegan Formation, Shaftesbury Formation, Labiche Formation). These are composed of quartz, with lesser amounts of feldspars and muscovite in the sand fractions, and kaolinite, illite, smectite, vermiculite and traces of chlorite in the clay fraction.

This brief summary indicates that kaolinite is the dominant phyllosilicate of the clay fraction of the bedrock within the study region, with lesser amounts of micaceous minerals, smectites, and trace amounts of vermiculite and chlorite. The sand fractions are composed primarily of quartz, with lesser amounts of feldspars and trace amounts of heavy minerals.

2.3 QUATERNARY SURFICIAL GEOLOGY.

Although the major physiographic features of the region are the result of the erosion of different bedrock lithologies during Tertiary and early Pleistocene time, the land was modified by continental glaciation during the late Pleistocene. The major spreading centres for the Wisconsinan ice mass affecting ice movement in the region were in in the Keewatin District (Gravenor and Bayrock, 1962). Virtually the entire region is covered by a veneer of unconsolidated glacial and derived postglacial deposits, varying from a few to several hundred meters in thickness (Hamilton and Mellon, 1973). Bayrock (1971, 1972a, 1972b, 1972c) and Bayrock and Reimchen (1974) have mapped the surficial geology of NTS sheets 74E, 74L, 74M, 74P and 84L at a scale of 1:250,000. MacPherson and Kathol (1977) reported on the surficial geology of potential mining areas

in the Athabasca Oil Sands region at a scale of 1:125,000. The surficial geology of the AOSERP study area has been mapped at 1:50,000 by Thompson *et al*. (1980). The deposits of importance to this study are summarised below.

During deglaciation, Glacial Lake McConnell was formed when the ice-front retreated north beyond Fort McMurray (Craig, 1965; Taylor, 1960). The lake was fed by the Athabasca River and by waters of Glacial Meadow Lake via the Clearwater and Athabasca spillways (Christiansen, 1979). The lacustrine sediments deposited in Lake McConnell, and the mixed lacustrine sediments described by McPherson and Kathol (1977) are grouped as one of the major parent materials described in this thesis, and are referred to as the Dover Unit. Soils of the Algar, Livock, Dover and Joselyn Soil Groups occur within this unit (Turchenek and Lindsay, 1981).

Glacial till is the common surficial deposit on the uplands within the study region. These deposits are thickest in the eastern and southern sectors of the area, and along the southwest flank of the Birch Mountains where accumulation may be to depths of more than 200 metres (Green *et al*. 1970; Bayrock, 1971). Bayrock and Reimchen (1974) recognised different till bodies based on matrix composition within the study region. Gypsy Till, composed mainly of quartzose sands from the Athabasca Formation, occurs to the east of the area, and grades into Kinosis Till, which has a loamy, gravelly and stoney composition, on the Muskeg and Stoney Mountain uplands and surrounding areas. These two till units comprise the Kinosis parent material unit, and are associated with the Kinosis Soil Group of Turchenek and Lindsay (1981).

Horse River Till, which has a clayey composition, occurs on the west flank of the Stoney Mountain upland, the Thickwood Hills, and underlies the lacustrine deposits of the region. Turchenek and Lindsay (1981) consider it to include any calcareous till found within the region. The Horse River Unit is associated with the Horse River Soil Group of Turchenek and Lindsay (1981).

The till on the Birch Mountains has a fine loam to clay matrix and contains much locally derived shaley material. This forms the Legend Unit of this thesis and is the parent material of the Legend Soil Group.

Other surficial units which have a marked difference in matrix composition are the sandy glaciofluvial outwash materials in the northeast of the study area. These materials

are not included in the clay mineralogical section of this study, but were utilised for the geochemical characterisation. Mineral soil parent materials are only exposed over approximately 50 per cent of the region with the remainder being blanketed by organic deposits (Turchenek and Lindsay, 1981).

2.4 SOILS INVENTORIES WITHIN THE REGION.

The soils studies the region have mainly been directed towards resource inventory. Lindsay *et al* (1957, 1961, 1962) classified and mapped soils at a 1:750,000 scale ,with unit separations being primarily based on parent material variation. Crown and Twardy (1970) mapped eight townships surrounding Fort McMurray at 1:126,720. Two of the oil sand leases were mapped; the Syncrude lease at 1:24,000 (Twardy, 1978) and Alsands at 1:20,000 (Hardy Associates Ltd, 1980).

Other soils related studies within the region have been directed towards reclamation problems following tar sand exploitation (McGill *et al*, 1978). Yeung (1980) examined the effects of acidification on Dystric Brunisols near Mildred Lake, and Parker (1979) examined the effects of emissions on throughfall and stemflow at several sites within the region.

3. CHARACTERISTICS OF SOIL MATERIALS OF THE INTERIOR PLAINS

This section of the thesis will briefly review literature with information describing the surficial materials of the Plains Region which is considered relevant to this particular study. The emphasis is on "soils" generated data in the clay mineralogical area because geological studies usually based interpretation on incomplete analyses. The relationships between soil composition and that of underlying bedrock formations was considered to be of paramount importance in the organisation of this review.

3.1 MINERALOGICAL CHARACTERISTICS:

Kodama (1979), in a literature survey of clay mineralogical data of Canadian soils, was able to relate the distribution of various clay fraction compositional assemblages to the soil-physiographic regions of Pettapiece (1976). Two of these regions, the Interior Plains and the Canadian Shield, are present in this study region. The general mineralogy of these regions is claimed to be similar because of the mixing during glacial transport (Kodama, 1979). The Interior Plains are dominated by smectite and mica, with mixed-layer clays being locally important nearer the Shield boundary, probably reflecting a contamination effect on the parent material in the marginal area. The data reviewed by Kodama (1979) indicated the subsoils of the Shield Region to contain abundant mica, followed in order by mixed-layer minerals, vermiculite, and smectite.

Before reviewing studies with data pertinant to parent material variation in Prairie soils, the statement in the introduction section concerning data reliability will be amplified by reference to a series of studies on the Cooking Lake Soil Series. All investigations were based on X-ray diffraction analyses and at least one of cation exchange capacity, total chemical analysis, differential thermal analysis, surface area and infrared spectroscopy for qualitative and quantitative estimates of the clay mineral assemblage. The main point of agreement among these studies (Pawluk, 1961; Kodama and Brydon, 1965; Twardy, 1969; McKeague *et al.*, 1972; Abder-Ruhman, 1980; Dudas and Pawluk, 1982) was on the dominance of montmorillonite and illite within the sediment. Acton and Crosson (1978), however, report montmorillonite and illite present in trace amounts only. The different kaolinite estimates are 10-35 % (Pawluk, 1961), a mean of less than 10 % for five different sites (Twardy, 1969), 5-20 % (McKeague *et al.*, 1972), trace amounts

only (Acton and Crossan, 1978) and 26 % (Abder-Ruhman, 1980). Twardy (1969) and Pawluk (1961) reported trace amounts of interstratified mica-smectite in the C horizons, wheras Kodama and Brydon (1965) reported 20 % of the same complex. This interstratified mineral was not reported at all by the other investigators, a fact confirmed by Dudas and Pawluk (1982) who demonstrated that only discete smectite and mica are present in this soil. Pawluk (1961) was the only one to report chloritic minerals, although Dudas and Pawluk (1982) suggest that trace amounts may be present. Abder-Ruhman (1980) claims, based on exchange capacity data, the presence of up to 10 % vermiculite, whereas Dudas (1982) states that another high-charge mineral, beidellite, is responsible for the K-fixation. Estimates of the amounts of quartz present in the clay fraction ranged from 2 to 40 %.

These qualitative and quantitative differences in the clay suite of this particular soil probably arise from differences in pretreatments of the clay separates used for X-ray identification and quantification. Although such interpretive variations are probably not unique, they certainly lend support to the plea by Srodon and Eberl (1980) for researchers to produce and publish X-ray diffraction patterns of high quality obtained by standardised techniques.

The most comprehensive study of surficial materials of the Interior Plains was published by Pawluk and Bayrock (1962). They found the content of montmorillonite in the clay fraction to incease from 20 % in the northern regions of Alberta to 60 % in central and southern regions; illite, at between 35 - 48 %, was most abundant in northern regions. The montmorillonite was described as being dioctahedral, with a composition somewhere between that of nontronite and beidellite. Kaolinite and quartz were present in minor amounts, and interstratified montmorillonite-mica was present in central and southern tills. Chlorite was observed in some samples, although no regional trend was apparent. A similar regional variation in sand mineralogy was described, with Na-Ca feldspars constituting 8.5 - 11.5 % of the sand fraction of tills in the north-central portion of the province, and 11.5 - 17.5 % in in the southern portion.

Twardy (1969) in a study of representative samples of parent materials from different tills, estimated montmorillonite species and illite to dominate the clay fraction (70 - 80 %), with minor amounts of chlorite, kaolinite and quartz constituting the

remainder. The light mineral (s.g. >>2.96) comprised 99 % of the sand fraction by weight, with 14 – 20 % being Na–Ca feldspar and 7 – 10 % being K–feldspar. The balance of this fraction was quartz; iron oxides and opaques were the major constituents of the heavy mineral fraction, with amphiboles and garnets being next in relative abundance.

Somasiri *et al* (1971), Somarisi and Huang (1973, 1974) presented a series of studies for a range of Saskatchewan soils in which they reported both dioctahedral and trioctahedral mica in the coarse clay, silt and sand fractions, but only dioctahedral mica in the fine clay. This is supported by the more recent findings of Abder–Ruhman (1980) in his examination of soils of East–central Alberta. Somarsi *et al* (1971), Somarsi and Huang (1973, 1974) indicate a higher proportion of dioctahedral mica in soils of the Southern Plains, a feature attributed to the higher proportion of Cretaceous bedrock incorporated into the tills. They also reported a decrease in the microcline to orthoclase ratio in the sand fraction of the soils towards the south of the transect which was related to the decreasing influence of material of Shield provenance. The increase in the orthoclase to microcline ratio as particle size decreased is probably because of the higher resistance of othoclase to glacial comminution, although the microcline is chemically less stable (Faure and Taylor, 1981). The various polymorphs, exsolution and order–disorder relationships of feldspar reported in the Saskatchewan pedons were also described by Abder–Ruhman (1980).

Acton and Crossan (1978) in the tour guides for the Eleventh Congress of the International Society of Soil Science presented results which appear incompatible with the balance of the literature describing the clay fraction of Prairie soils. They describe quartz as being dominant in the clay fraction of Alberta soils, with mica being present in trace amounts only. Kaolinite, chlorite and vermiculite were reported in trace amounts, whereas quartz was documented as being as high as 20 – 40 % of this fraction.

Dudas (1968) and Dudas and Pawluk (1970) describe a series of pedons in central and southern regions of Alberta. The clay suite of the C horizons was dominated by montmorillonite. Kaolinite and chlorite were present in lesser amounts (less than 10 %), and at some sites randomly–interstratified illite and montmorillonite species were identified. However Dudas and Pawluk (1982) modify some of their earlier estimates of

relative composition based on a more complete set of pretreatments of samples prior to X-ray diffraction analysis. The most significant changes being that the interstratified minerals are absent (Pawluk, 1961; Kodama and Brydon, 1965; Dudas, 1968; Twardy, 1969; Dudas and Pawluk, 1970), and the differentiation of the smectite component into two species, beidellite and montmorillonite. Dudas and Pawluk (1981) state that dioctahedral mica is more abundant than trioctahedral, and that the chlorite species in the tills is iron-rich. There is also the suggestion, noted earlier in this discussion, that the vermiculite of Abder-Ruhman (1980) may be beidellite.

The theses of both Howitt (1981) and Abder-Ruhman (1980) confirm the dominance of smectite in both the Breton and Cooking Lake tills, with mica and vermiculite being associate minerals. Abder-Ruhman reports up to 30 % kaolinite in samples from east-central Alberta. The X-ray diffractograms presented by Howitt (1981) indicate a significant kaolinite component in the clay separates of the Breton till. Howitt (1981) reports the possible presence of nontronite based on chemical analysis, and soil vermiculite, a dioctahedral smectite with hydroxy-Al as an interlayer component (Rich, 1968), based on the lack of expansion of the 10 A° peak on rehydration of a K-saturated sample. Trace amounts of quartz and amorphous materials were also described in the parent materials of both studies. Sand fractions contain up to 50 - 75 % quartz, up to 6 % alkali feldspars and 12 % plagioclases, and a dominance of opaque minerals, haematite, amphiboles and garnet in the heavy fraction.

A series of studies on Solonetzic and Chernozemic soils on the sediments of the Lake Edmonton basin (Arshad and Pawluk, 1961; Sanborn, 1981) indicate a dominance of smectite and mica in the clay fraction, with lesser amounts of kaolinite, chlorite and quartz. Arshad and Pawluk (1966) report the presence of interstratified minerals, and describe the smectite as a transitional phase between nontronite and beidellite. Sanborn (1981) suggests a possible presence of vermiculite. Composition of the sands in these studies is 75 % quartz, 10 - 20 % soda-calcic feldspar and up to 10 % K feldspar. The heavy mineral composition is similar to that reported for tills of the region, with the exception of lesser amounts of hornblende. Data of Rice (1959) for glaciolacustrine soils of Alberta and Saskatchewan indicate composition similar to that described above.

Parent materials of soils developed on "acid" shales in Northwest Alberta (Pawluk and Dudas, 1978) was quite different from any described above. The clay suite was dominated by dioctahedral mica and kaolinite, with a lesser amount of soil-vermiculite and a trace of chloritic intergrade. Pawluk (1961, 1971) and Lavkulich *et al* (1964) report data contrasting to the above for soils developed on glacial deposits in the same region. The clays are described as being dominated by smectite and mica, with significant amounts of kaolinite and chlorite. The sand composition is similar to that reported elsewhere, namely quartz 70 - 85 %, Na-Ca feldspar 10 - 20 %, and K feldspar 5 - 9 %.

Podzolic parent materials of Northeastern Alberta had a clay assemblage dominated by illite, mixed layer montmorillonite-illite, discrete montmorillonite and kaolinite (Pawluk, 1960). Analyses of Brunisolic soils near Lake Claire (Pawluk and Lindsay, 1964) show variable amounts of montmorillonite, a major component of illite, with significant amounts of kaolinite, chlorite and mixed layer clays. The sand fractions show a dominance of quartz, with lesser amounts of Na-Ca feldspar, K feldspar and minor amounts of heavy minerals.

One of the major problems in the description of clay mineralogy in these studies has been that of terminology, especially for the smectite minerals. Smectite is the correct group name for the 2:1 clay minerals with the terms montmorillonite, beidellite, nontronite being species names which define the compositional series of this dioctahedral mineral group. The researchers discussed here often used the term montmorillonite as a synonym for smectite, and then proceed to discuss a montmorillonite-beidellite composition, a beidellite-nontronite composition, generally without presentation of supporting evidence. These individual mineral species have relatively narrow compositional ranges and cannot generally be differentiated within the smectite group unless samples are analysed following a range of solvation and hydration treatments. Unless uniform standards of analysis and interpretation are adhered to, many of the regional surveys, as attempted here, are of limited value. A similar terminology problem exists with the term illite -- a researcher must define the criteria on which he bases his interpretation. However, comments such as the above must be tempered with the realisation that clay mineralogical research and definition has been developing over the past 35 years, and many of the general classification criteria have only recently

become standardised. It is unfortunate that the standard criteria defined by the various international clay nomenclature committees are not yet generally adhered to.

The above comments do not alter the general conclusions of Kodama (1979). The clay mineral components of the subsoils of the Interior Plains appear to be dominated by smectite minerals, with slightly lesser amounts of micaceous minerals, and minor levels of kaolinite and chlorite. Regional variation is not readily apparent, with the exception of the study of Pawluk and Bayrock (1969), but this may be more the result of the lack of uniformity of the analytical criteria, than a product of the glacial mixing pot. The Shield region has no published data for the region adjacent to Northern Alberta, thus no general statement can be made concerning mineralogical composition or variation.

3.2 CHEMICAL CHARACTERISTICS:

McKeague *et al* (1979) compiled much of the published data in conjunction with their studies of background levels of minor and trace elements in Canadian soils. They describe levels for 53 profiles both on a national and regional basis. The mean levels documented are: Cr 43 (38), Mn 520 (377), Co 21 (15), Ni 20 (18), Cu 22 (21), Zn 74 (64), Sr 210 (174), Hg 0.06 (0.04), Pb 20 (15). Values are in ug gm^{-1}, with those in brackets representing means of data for samples from the Interior Plains region. Their data compare closely with data reported for levels in soils of the U.S.A. (McKeague and Wolynetz, 1980). However, they report data for only 17 sites for the entire Interior Plains region, and document no sites within the present study region. Their prediction of levels in the entire region is thus based on this small sample base on the Eastern limits of the region.

Webb and Howarth (1979) point out that extrapolation of the results of detailed studies from such type localities ignores the often significant differences in composition within single stratigraphic formations which are lithologically different in space. Such comments tend to temper the statement of Dudas and Pawluk (1980) that predictions of elemental status of soil material can be based on average values of parent rocks. This is complicated, even if the parent lithology is uniform, by changes in composition owing to sedimentary source variations and/or selective mobilisation and redeposition of individual elements during weathering processes (Webb and Howarth, 1979). This is further

compounded by the vagaries of glacial/fluvial/aeolian processes on surficial materials within Western Canada.

The approach investigated by the U.S. Geological Survey, in conducting a reconnaissence geochemical survey of Missouri State, was based on random sampling of previously mapped broad geological, pedological, vegetational and hydrological units at different densities (Tidball, 1972; Miesch, 1976; Erdmann *et al.*, 1976). Analyses of variance was used to study geochemical variation between each selected unit, and it was found, for many of the 30 – 40 analysed elements, that significant differences occurred between the previously mapped surficial units. These techniques were deemed suitable for regions containing relatively homogeneous pedologic units, such as may be associated with glaciated terrain.

The regional geochemistry of Alberta was mapped, at an average sample density of one sample per 10 townships (Bayrock and Pawluk, 1967; Pawluk and Bayrock, 1969), and presented as maps for about 65 % of the province. The authors concluded that much of the regional variation was a result of incorporation of bedrock materials into the tills. Regional highs of combinations of Fe and Cu, which were most concentrated in the north west, could be used to differentiate bedrock subcrop patterns. The reported concentration ranges were Cu 5 – 40 ug gm^{-1}, Fe 2 – 4 %, Zn 50 – 70 ug gm^{-1}. They suggested that CaO levels could be used to delineate patterns of glacial advances, especially in the north east of the province. Content of other elements reported were B 13 – 70 ug gm^{-1}, Co 2.5 – 11 ug gm^{-1}, Mn 0.008 – 0.055 %, and Mo <1 – 3 ug gm^{-1}. In a regional mapping of overburden materials, the glaciated terrain of Southern Saskatchewan was found to have the following levels in the C horizons: Al 5.3 %, Hg 26 ppb, Mn 440 ug gm^{-1}, Ni 22 ug gm^{-1}, Si 27 %, Sr 240 ug gm^{-1}, V 64 ug gm^{-1} (Severson and Tidball, 1976). These levels are comparable to those from the glaciated regions of Missouri presented by Erdman *et al* (1976). Additional elements described in the latter study pertinent to this thesis are: As 13 ug gm^{-1}, Cr 66 ug gm^{-1}, Cu 24ug gm^{-1}, Fe 3.5 %, K 1.5 %, Mg 0.54 %, Mo 3 ug gm^{-1}, Na 0.5%, P 0.033 %, Ti 0.37 %, and V 110 ug gm^{-1}. However,differentiation between various levels of the Soil Taxonomy (Suborders, Subgroups and Series) using such data was only regionally applicable at the series level. At higher levels of abstraction, the significant differences were only found

to account for 35 – 45 % of the natural variation.

Doyle (1977), Doyle and Fletcher (1977, 1979) applied the statistical design of Miesch (1976) to analyse regional variation in minor element composition of soil parent materials in Central Alberta and Saskatchewan. They found that up to 78 % of the soil data variance could be attributed to differences among parent materials. The elemental concentrations for the four elements analysed (Cu, Fe, Mn, Se, Zn) in C horizons was highest in lacustrine clays, lower in glacial till and alluvium, and lowest in aeolian deposits.

The natural abundance of several trace elements in Chernozemic and Luvisolic soils of Alberta was examined by Dudas and Pawluk (1980). The mean data of relevance to this study are : As 5.8 ug gm^{-1}, Cu 22 ug gm^{-1}, Pb 16 ug gm^{-1}, Zn 59 ug gm^{-1}. They also examined concentrations in size fractions for the same elements and found the following for the clay separates: Cu 44 ug gm^{-1}, Pb 25 ug gm^{-1}, Zn 126 ug gm^{-1}.

McKeague *et al* (1979) used the data obtained in their compilation to calculate prediction equations for minor elements based on more easily determined parameters such as clay, organic C and the major elements (A1, Fe, Ca, Mg) as independent variables. They were able to account for more than 50 % of the variability of Mn, Cu, Pb, Co, Ni, Cr, Sr and Se in this for manner for different sample groupings. Such relationships are obviously based on the ability of the minor elements to proxy for the macroelements in the crystal lattices of various minerals (Dudas and Pawluk, 1980). They were able to predict Sr levels based on Ca alone for non–calcareous samples, probably because Sr can proxy for Ca in pl agioclase feldspars (McKeague and Wolynetz, 1980)

Geochemical exploration work has produced a vast body of data in regions of known mineralisation, much of which is not pertinent to this study because the determinations are made on a range of size fractions, rather than < 2mm material. Data of relevance to the 2um fraction will be mentioned here. Shilts (1977), in a study of 1000 till samples from the Keewatin region, describes the content of the following in the clay separate: Zn 100 ug gm^{-1}, Cu 100 ug gm^{-1}, Ni 80 ug gm^{-1}.

This review has shown that, although there is a considerable amount of site specific data on levels of minor elements in soils in Canada, there are very few studies describing regional variation of major, minor and trace elements Studies relating concentrations of specific elements to parent material variation are similarly sparse, and

there is only one detailed study of elemental partiti ioning among the various particle size fractions of soils, although this does, admittedly, discuss the data with genetic overtones.

4. NUMERICAL CLASSIFICATION IN SOILS

There are only a handful of publications specifically related to pedological problems, with the majority of these being used to analyse the regional variation of soil properties as related to predetermined classification system. Progress in the numerical classification of soils tends to support the potential cited by Whitehead (1925):

> Classification is necessary. But unless you can progress from classification to mathematics, your reasoning will not take you very far.

Sneath and Sokal (1962) define numerical taxonomy as the numerical evaluation of the affinity or similarity between taxonomic units and the ordering of these units into taxa on the basis of their affinities. They further state that it draws on Adonsonian principles of taxonomy which can be outlined as follows:

1. Ideal natural taxonomy is one in which taxa have the greatest content of information.
2. Every natural feature is of equal weight in constructing a classification
3. Affinity is a function of proportion of features in common.
4. Affinity is independent of phylogeny.

Thus, using these principles, numerical taxonomy has a quantitative basis (Buol *et al*, 1980), and produces a phenetic classification, ie. one based on property similarity (Mikhaylov, 1973). Detailed reviews of the mathematics involved in these techniques can be found in Mikhaylov (1973), Arkley (1976) and Webster (1977).The most important facet of numerical classification is that characters are given equal weight in computational procedures (Sokal and Sneath, 1963), a facet which does not rest well with the traditional pedologist.

This problem was evaluated by Sarkar *et al* (1966) by examining the the product-moment correlation coefficients computed for 61 properties from 26 profiles. They were able to remove, based on correlation coefficients, 39 of the variables with only minor alteration to the resultant profile classification dendrogram produced by cluster analysis. An example of their data reduction is the removal of 5 of their initial 6 particle size ratios because of intercorrelation above the 0.90 level.

Earlier attempts at numerical classification were based on application of Q-mode ordination (Hole and Hironka, 1960;Bidwell and Hole, 1964). These workers calculated

indices of similarity, the former on three groups of soil profiles from a catenary sequence and the latter on a group of 30 soils representative of the major soil orders in Kansas. Models constructed by Hole and Hirjonka (1960) for laboratory and morphological data independently were visually very similar, but displayed how combinations of properties from a catenary sequence displayed individual groupings compared to real landscape variations based on property interrelationships. They extended their basic model to cover a range of 25 profiles from major Great Groups and concluded that ordination provided insight into confirming or testing hypotheses of pedologists. The ordination of Kansas soils (Bidwell and Hole, 1964) substantiated the intuitive classification and preconceived concepts of property interrelationships between the soils. The major problem discovered was related to choice and weighting of characteristics, a problem which can remove some of the objectivity from the resultant classification.

Application of ordination techniques have turned from the methodology used by Hole and co-workers to vector methods such as Principal Component Analysis, and Principal Factor Analysis. These have proved to be most valuable for exploring relationships among soil profiles. The procedure has been reviewed in detail by Webster (1975, 1979). Examples of the use of Principal Component Analysis for display and interpretation of relationships in multivariate soil populations are found in papers by Cuanalo and Webster (1970) and Areola (1979). Both of these studies followed the interpretation of the Principal Component Analysis with a grouping technique to produce a classsification dendrogram based on the Euclidean distance between cluster centroids and individual samples. The first two components produced by the ordination were interpreted by Cuanalo and Webster (1970) as being related to water tension, structure strength and texture; results from the clustering analyses of Brown Earth and Gley profiles in the data set showed strong differentiation between the groups, with sub-clusters showing relationships of individual properties within the groups. The ordination analysis of Areola (1979) produced components which could be intuitively related to organic matter, pH, texture and base status. The grouping from cluster analysis did not correspond with a natural classification, or with a land-facet classification, but grouped soils with similar parent materials, hydrological characteristics and organic

matter relationships. These groupings were obviously related to drainage conditions, lithology and surface organic matter accumulation.

Barkham and Norris (1970) used Principal Component Analysis on both vegetation and soils to examine the relationships between the two by comparing the first two vegetative components with four soil components and related soil variables, and by canonical correlations between componenents of the two systems. They considered this procedure to provide a workable strategy for investigations of such complex systems. Modifications of this approach were used recently for examination of soil–vegetation relationships (Moon and Seldy, 1980) in British Columbia, as an aid in definition of ecologically–based mapping units. Norris (1972) found Principal Component Analysis results useful in solving applied problems in soil mapping and classification, and suggested usefulness as an aid to understanding causes of soil variation. Webster (1978) and Webster and McBratney (1981) used Principal Component Analysis and canonical variates to first simplify soil data, and then partition transects based on the minimized withinsegment sum of square deviations from segment means.

Arkley (1968, 1971) used the allied Principal Factor Analysis to produce dimensionless factors which were independent of each other, and which contained from two to four highly correlated soil properties. The major observation was that, with six different data sets being used, the same general definitive criteria were selected as members of the individual factors. Subsequent cluster analysis based on the chosen variables produced a classification for the various data sets which was closely allied to that obtained using the 7th Approximation. He thus concluded that such non–Linnean taxonomic systems based on a co–ordinate classification of a few statistically chosen factors would be a suitable basis for a non–dichotomous soil taxonomic system, especially as soils have no real genetic heredity. Nortcliff (1979) used Principal Factor Analysis to minimize the number of variables for further analysis and to ascertain the variance within parent material parameters of individual map units.

A traditional and problematical task in soil survey is the allocation of individual profiles or sites into the most appropriate classes of an existing scheme of classification (Webster and Burrough, 1974). Discriminant function analysis is one solution to this allocation problem. It has been used for geochemical data (May, 1972), for soil survey

data (Webster and Burrough, 1974), for description of soil taxonomic units (Ragg and Henderson, 1980a, 1980b), to ascertain membership of stages of a chronosequence (Berg, 1980) and to distinguish between soil features related to occupation at an archeological site in Ontario (Griffith, 1981). This method of analysis is also useful to evaluate the best pedogenic or chemical variables for distinguishing between *a priori* groups; these groups may have been defined intuitively or by techniques such as cluster analysis.

Although the emphasis of the preceeding discussion has been on the application of techniques for numerical classification, no mention has been made of application problems. Webster (1981) describe Principal Component Analysis as a disinterested way of condensing multivariate data with the maximum amount of information being contained in the leading components, whether or not all of this information is necessary for class distinction. He suggests use of canonical correlation which generally presupposes class distinction and concentrates discriminating power into the leading variates. Hawkins and Merriam (1974) demonstrated that this technique may be applied for sites from an ordered series (eg. asoil transect) without prior grouping.

The development of numerical classification methods has stressed equal weighting of all properties (Sokal and Sneath, 1963) and mention has been made of attempts to avoid inadvertant weightings of inherently correlated properties (Sarkar *et al*, 1966). Kloosterman and Lavkulich (1973) considered that, because soil is the expression of a great number of interrelated properties, it is difficult to justify deletion of any of these merely on the basis of significant correlations. They suggest inadvertent weighting of primary and secondary expressions can be avoided by careful study of any selected variable set, a suggestion which removes much of the objectivity from the analytical approach. A major problem in the opinion of the author is that reseachers expect the classification results to substantiate the initial biases developed during data collection, or imposed by an external hierarchical classification system. The results of numerical taxonomy should be applied as an aid to understanding the system under examination.

Complete objectivity in classification is unattainable and systems of classification, whether numerical or traditional, will always be to some degree subjective. The theory dependent traditional soil classification systems are more likely to be objective than the

numerical systems (Muir *et al*, 1970). The value of using computers is not so much in devising systems, but in the fact that, once programmed, they act without bias. This lack of bias is particularly valuable because even the best classification of a series of individuals will be subjective, and thus must be applied objectively (Muir *et al*, 1970).

5. SAMPLES AND METHODOLOGY

5.1 SAMPLE SELECTION AND PREPARATION.

5.1.1 Field Sampling

A total of 100 soil parent material samples (CSSC, 1976) were collected in the summers of 1977–78 from within the AOSERP study area. The samples were chosen and collected, after extensive field checking during the course of a reconnaissence soil survey, to represent the modal concepts of the different Soil Units. The major Units, namely Kinosis, Legend, Horse River and Dover were represented by at least 11 samples per unit, whereas some of the the other Soil Units were sampled only twice.

All samples were taken from the C horizon (CSSC, 1976), at depths of between 1 and 1.5 metres. At each site field characteristics were described (Table 1), and a 3 kilogram sample was collected. Samples were generally collected from well-drained topographic positions.

5.1.2 Sample Preparation

The bulk samples were air dried at room temperature, and fragments larger than 5 mm. were manually separated. The remainig material was ground to pass a 2mm. sieve, and stored for subsequent analysis.

5.2 ANALYSES OF WHOLE SOIL SAMPLES

Chemical and physical analyses were conducted using the routine procedures of the Alberta Institute of Pedology. These included:

1. Particle size distribution by the pipette method. Sands were dry sieved using a sonic sifter.
2. Soil reaction was determined using both water and 0.01 M $CaCl_2$ in a 2:1 ratio of solution to soil.
3. Calcium carbonate equivalent was determined by the manometric method.
4. Total carbon was determined by dry combustion using an induction furnace with

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Table 1: Legal location and field charactristics of the sample sites.

Sample Number	Location	Parent Material	Texture	Colour (m)	AOSERP Soil Unit
1	NW10- 92-11	Lg	cl	10YR4/3	JSN1
2	SE28- 92-12	Lg	c	10YR3/3	JSN1
3	SW17- 94-11	Lg	scl	10YR4/2	JSN1
4	NW17- 97-12	Lg	cl	10YR3/2	DOV1
5	NE11- 87-10	Lg	cl	10YR3/3	DOV1
6	NW 7- 91-10	Lg	cl	10YR4/3	JSN1
7	SW26- 88- 9	Lg	c	10YR4/2	DOV1
8	NW29- 96-12	Lg	cl	10YR3/3	DOV1
9	NE 2- 87- 9	Lg	cl	10YR3/3	DOV1
10	SE 9- 94- 6	M	fsl	10YR4/3	KNS1
11	SW25- 95- 6	M	fsl	10YR3/3	KNS1
12	SE34- 92- 8	M	fsl	10YR3/3	KNS1
13	NW10- 93- 6	M	fsl	10YR3/3	KNS1
14	SW32- 92- 4	M	l	10YR3/3	KNS1
15	NW12- 87- 7	M	scl	10YR3/3	HRR1
16	SE35- 84- 9	M	l	10YR4/2	KNS1
17	SW 8- 82- 7	M	l	10YR4/2	KNS1
18	NE31- 83- 6	M	l	10YR3/3	KNS1
19	NE18- 85- 8	M	scl	10YR3/3	KNS1
20	NW 8- 90-12	M	l	10YR3/3	HRR1
21	NW25- 91-10	M	fsl	10YR4/4	HRR1
22	NE 6- 91-18	M	l	2.5Y4/2	HRR1
23	NW 2- 90-14	M	l	2.5Y4/2	LVK1
24	SW 2- 88-16	M	l	2.5Y3.5/3	HRR1
25	NE 3- 88-18	M	hc	2.5Y3.5/2	HRR1
26	NW14- 95-16	M	cl	2.5Y3/2	HRR1
27	NE 8- 95-18	M	cl	10YR3/2	LGD1
28	NW23-104-15	M	cl	10YR5/1	LGD1
29	NE23-103-18	M	sic	10YR4/2	LGD1
30	NE29- 97-18	M	sic	10YR3/2	LGD1
31	SW24- 98-17	M	cl	10YR3/1	LGD1
32	SW18-100-17	M	scl	10YR3/2	LGD1
33	SW14-102-17	M	sic	2.5Y3/2	LGD1
34	SE11- 97-15	M	l	10YR5/3	LGD1
35	SW 8- 99-14	M	l	2.5Y4/2	LGD1
36	NE13-100-15	M	hc	5Y4/2	LGD1
37	SW 8-100-15	M	sic	5Y3/1	LGD1
38	NE18-100-15	M	cl	10YR3/3	LGD1
39	NW 9-100-12	M	l	10YR3/3	LGD1

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Table 1: Legal location and field charactristics of the sample sites (continued).

Sample Number	Location	Parent Material	Texture	Colour (m)	AOSERP Soil Unit
40	SW10- 95- 8	Lg	l	10YR3/3	DOV1
41	NE 8- 84-11	M	cl	2.5Y3.5/2	SRT1
42	NE 8- 83-13	M	l	2.5Y4/2	SRT1
43	85-14	Lg	cl	10YR4/3	DOV1
44	91-13	Lg	cl	10YR4/2	DOV1
45	92-18	Lg	scl	5YR4/2	DOV1
46	89-17	Lg	cl	10YR4/2	DOV1
47	88-19	Lg	c	10YR5/2	JSN1
48	NW 2- 86-17	E	fs	2.5Y4/2	HRT4
49	SE33- 86-12	E	fs	2.5Y4/2	LVK
50	NW16- 95- 4	M	l	10YR5/4	KNS1
51	22-103-11	F	fsl	10YR5/4	NAM2
52	NW20-102-13	M	sl	10YR5/6	LGD1
53	NE 8-109- 9	F	sicl	2.5Y5/2	CPN1
54	NW24-108- 8	F	fs	10YR4/3	CPN1
55	NE16-109- 8	F	fs	2.5Y5/4	CPN1
56	NE24-109- 8	F	sic	2.5Y3/2	MMW2
57	NE15-109- 7	F	l	2.5Y4/2	CPN1
58	NW 8-107- 9	F	l	2.5Y6/2	CPN1
59	SW20-104- 6	Fg	s	5YR6/3	FIR1
60	8-102- 9	Fg	s	5YR6/3	FIR1
61	NW21- 95-12	Lg	c	10YR4/2	JSN1
62	NW32- 93-10	Ev	s	10YR4/6	HRT4
63	NE13- 99-11	F	sl	10YR3/2	NAM2
64	NE13-100-12	M	l	10YR3/3	BKN1
65	NW12- 97- 7	Fg	sl	10YR4/3	FIR2
66	SE10- 98- 4	Fg	s	10YR5/4	FIR1
67	NE30- 98- 5	M	cl	10YR4/4	KNS1
68	12-100- 8	Fg	s	5YR6/3	FIR1
69	SW11- 97-10	M	cl	10YR3.5/3	HRR1
70	NE31- 96- 9	Fg	s	10YR3/3	FIR2
71	NW 9-100-12	M	s	10YR4/4	FIR1
72	SE19- 93-10	Fg	sl	2.5Y5/2	MIL1
73	SE25- 91-10	M	scl	10YR4/4	HRR1
75	NE11- 87-10	Lg	l	10YR3.5/3	DOV1
76	SW25- 88- 8	M	ls	10YR5/6	RUT1
78	SE 8- 89-12	E	ls	5YR5/8	HRT5
79	31- 89- 7	M	c	10YR4/4	KNS1
80	SE26- 89-10	Lg	cl	10YR3/4	DOV1
81	NW26- 89-10	Lg	c	10YR4/3	DOV1

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Table 1: Legal location and field charactristics of the sample sites (continued).

Sample Number	Location	Parent Material	Texture	Colour (m)	AOSERP Soil Unit
82	SW24- 88- 4	M	scl	5YR5/6	RUT1
84	18- 89- 8	Lg	c	10YR5/8	RUT1
85	SE 3- 90- 8	Lg	cl	10YR4/4	DOV1
86	NE 8- 89- 8	Fg	sl	10YR4/4	HRT5
87	SE24- 88- 7	M	l	10YR3/4	RUT1
90	94-13	Lg	cl	10YR4/3	
91	93-15	Lg	cl	10YR4/3	
92	90-16	Lg	cl	10YR4/2	
93	SW19- 92-12	Lg	scl	10YR4/3	JSN1
94	NW13- 99- 6		sl	10YR2.5/2	STP1
95	SE22- 94- 8		cl	10YR6/2	STP1
97	22-105- 6	E	s	10YR7/4	HRT6
98	NW14- 97- 8	Fg	sl	10YR5/4	BMT1
99	SW32- 86- 8	Lg	cl	7.5YR4/2	KEL1
100	NW 4- 95-15	M	scl		MKW1
101	SE28- 99-13	M	sil		MKW1

gasometric detection of evolved CO_2 (Leco Model 577-100).

5. Exchange Capacity was calculated by displacement of ammonium with sodium chloride.

6. Exchangeable cations were measured following displacement with ammonium acetate at pH 7. The displaced K, Na, Mg and Ca were determined by AAS.

5.2.1 Sample Geochemistry

Subsamples were ground in a swing-mill and dissolved by HCl-HF treatment (Pawluk, 1967). The resultant solutions were analysed for Al, Ca, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, P, Pb, Sr, V, and Zn by ICP-AES (Appendix VII). Ti and Ni were determined by AAS, and Si was calculated by difference. As was determined on selected samples by the semimicro colourimetric technique of Small and McCants (1961). The flameless atomic absorption method of Melton *et al* (1971) was used to determine total Hg on these same selected samples.

5.3 MINERALOGICAL ANALYSES

A total of 46 samples representive of the Dover, Kinosis, Horse River and Legend Soil Units were selected for detailed mineralogical analyses. A sample- -splitter was used to obtain a representative 50 - 75 grams of the less than 2 mm soil material. Sand, silt , and clay fractions were separated from the samples by wet sieving, gravity separation and centrifugation techniques (Jackson, 1975). The samples were dispersed in distilled water using ultrasonic vibration without pretreatment to remove organic matter or carbonates. Separated clay in suspension was flocculated with $CaCl_2$, then washed free of excess chloride with distilled water, and centrifugation. The clay fractions were freeze-dried prior to subsequent analyses, and silt and sand fractions were dried at 50 °C.

5.3.1 Sand Mineralogy

The fine sand fraction (50 – 250 um) was separated into heavy (S.G.>2.73) and light fractions (S.G.< 2.73) using a tetrabromoethane / bromoform mixture (Carver, 1971). Subsamples of the <2.73 separate were dissolved with HCl – HF (Pawluk, 1967) and analysed for Na^{+}, K^{+}, Ca^{++} and Al^{+++} by atomic absorption spectrometry, with the resultant data being used to calculate contents of Na–, K–, and Ca–feldspar. The theoretical Al^{+++} was determined from the formulae weights of the above feldspars in order to assess the level of any calcareous impurities. A relatively pure concentrate of K–feldspar was obtained by further density separation (2.73 – 2.59). This concentrate was crushed and analysed using a Philips diffractrometer utilising Cu K–alpha radiation, at a scanning speed of $^{1}/_{3}{}^{0}$ 2 θ min^{-1}.

Selected samples of the 2.73 – 2.59 and <2.59 density separates were examined with a Cambridge Stereoscan S 4 scanning electron microscope, in order to describe surface micromorphological features. The samples were coated with 100 A^{0} of Au in an Edwards Sputter Coater. Qualitative chemical spectra of individual grains were obtained using a Kevex 7000 Energy Dispersive X–ray analyser and compared with those of pre–analysed standard minerals to aid positive species identification.

Grain mounts of all separates were prepared by impregnation of sample fractions in small aluminium holders with 3–M Scotchcast Electrical Resin, No. 3. These were mounted on standard petrographic slides (27 * 46 mm.) and ground to a thickness of 30 microns. Standard optical petrographic techniques (Kerr, 1977) were used to indentify individual minerals.

5.3.2 Clay Mineralogy

Slides of Ca^{++} and K^{+} saturated slides were prepared using the paste method of Theissen and Harward (1962). X–ray diffraction analysis was performed with a Philips Diffractometer equipped with a curved crystal monochrometer, using Cu K alpha radiation. Ten pretreatments as outlined below, with the sample chamber maintained at the specified humidity levels.

1. Ca^{++} saturated, 54 % relative humidity
2. Ca^{++} saturated, ethylene glycol solvated.

3. Ca^{++} saturated, glycerol solvated.
4. K^{+} saturated, heated to 105 °C, 0 % relative humidity.
5. K^{+} saturated, heated to 105 °C, 54 % relative humidity.
6. K^{+} saturated, heated to 300 °C, 0 % relative humidity.
7. K^{+} saturated, heated to 550 °C.
8. Li^{+} saturated, heated to 200 °C, 0 % relative humidity.
9. Li^{+} saturated, heated to 200 °C, glycerol solvated.

Cation exchange capacity was determined by extraction of Ca^{++} saturated clays with 2 N KOAc, and measurement of displaced Ca^{++} (CaEC) by AAS. After washing with water / alcohol mixtures, the sample was extracted with 2 N NaOAc and the displaced K^{+} measured to provide a measure of KEC. A short sonication treatment was utilised during both extraction procedures to ensure complete replacement of the saturating cations.

Surface area was measured by the ethylene glycol monoethyl ether method (Carter *et al*, 1965), with the modification that samples were equilibrated with EGME vapour rather than saturated with EGME followed by desorption of excess liquid.

Dissolution of Ca – saturated clays was conducted as described by Pawluk (1967). The solutions were analysed for 18 elements as outlined in Appendix VII. Si was calculated by difference, with the values for some samples being checked by direct aspiration of clay suspensions (Appendix VIII).

Infrared spectra were obtained for selected representative fine, coarse, and bulk clay separates using a Beckman IR – 20 Infrared Spectrometer. Approximately 4 mg. of clay were pressed into a KBR disc, heated to 200 °C to remove adsorbed water, and repressed prior to analysis. Spectra were obtained using a scan speed of 240 $cm.^{-1}$ $min.^{-1}$.

An Aminco Thermal Analyser, Model 4–4442, was used for differential thermal analysis of selected bulk and fine clays, with calcined alumina used as a reference material. Samples were usually Ca – saturated, but some fine clays were saturated with piperidine (Allaway, 1948; Oades and Townsend, 1962) to aid in smectite species identification.

Representative samples of the bulk clay separates from the Kinosis, Legend and Horse River Units were analysed for ^{18}O content. Prior to analysis the organic matter was

removed from these samples by treatment with sodium hypochlorite (Lavkulich and Wiens, 1970). Amorphous clay material was then removed by boiling in 0.5 N KOH (Dudas and Harward, 1971). The clay separates were then oven dried at 100 °C , and heated in a vacuum at 200 °C to remove the interlayer water. Oxygen was liberated from the samples by reaction with fluorine (Taylor and Epstein, 1962), and analysed for ^{18}O content by mass spectrometry. Isotopic data are reported in alpha-notation, as deviations of the isotopic composition in parts per thousand ($^{0}/_{00}$) from that of the SMOW standard (Craig, 1961).

5.4 NUMERICAL CLASSIFICATION TECHNIQUES

The chemical and geochemical data obtained in this study were subjected to analysis by techniques described as numerical classification by Webster (1979). The purpose of numerical classification is to produce groups which are as homogeneous as possible within the groups, but are as distinct as possible between the groups. To achieve this purpose, a measure of similarity is used to objectively evaluate the similarity or dissimilarity between the individuals; then another measure of similarity, called a sorting strategy, is applied to form groups. This process of grouping individuals on the basis of similarity or dissimilarity is called classification (Sokal, 1966).

Studies which examine relationships between variables are called R-mode analyses, whereas investigations of between individual relationships are called Q-mode analyses. Classification can be utilised to identify generic units for mapping purposes (Volland and Connelly, 1978). The classification phase may be hierarchical or reticulate, and may also be divisive or agglomerative in the way groups of similar individuals are formed. Finally, the classification may be based on monothetic or polythetic procedures. Webster (1979) indicates that hierarchical agglomerative procedures, although they may not perform optimally on poorly structured populations such as soils, are the most popular in pedological studies and are, by nature, polythetic.

The coefficients used in numerical classification can be grouped into three catagories (Williams and Dale, 1964):

1. Information statistics.
2. Euclidean distances.

3. Disjoint – space functions.

Information statistics are used in conjunction with either presence–absence or continuous data, and are considered non–metric and non–Euclidean. Euclidean distance statistics are metric, and measure the distance in space between two individuals, or between a cluster of individuals and other individuals. Use of Euclidean distance metrics requires an assumption that the variables are uncorrelated. Pyott (1972) notes that Euclidean distance is biased towards attributes which are highly variable across the data set, and the resulting classification will be regulated by the more abundant rather than the diagnostic attributes. This tendency may be alleviated by data standardisation. Disjoint–space functions use a probablistic approach to classification in which a null hypothesis is required, and thus an assurance that the data follows some known probability distribution is required (Williams and Dale, 1965).

In a study of soil trace element data, Moore and Russell (1967) indicate that Euclidean distance coefficients possess the following advantages :

1. They are metric.
2. They are likely to separate groups with aberrant attributes.
3. They provide models which may be grasped mentally with comparative ease.

For these reasons the Euclidean distance coefficients are used in this study.

5.4.1 Cluster Analysis

Cluster analysis is a term applied to a host of methods used to combine either individuals or groups in either a hierarchical or a reticulate classification. As hierarchical classification optimises a route between a population and its individuals (Volland and Connelly, 1978), it is used in this study. Different classifications result from the application of different clustering techniques to the same transformation matrix (Williams, 1971).

The most common hierarchical clustering strategies as outlined by Webster (1979) are :

1. Single linkage grouping (nearest neighbour).
2. Centroid method.
3. Weighted centroid method.

4. Group average method.
5. Complete linkage grouping (farthest neighbour).
6. Flexible grouping.
7. Ward's method.

As is indicated by Webster (1979), it was necessary to perform analyses by several of the above methods to ascertain the degree of clustering exhibited by the data generated in the course of this study.

5.4.2 Discriminant Analysis

Discriminant analysis is utilised in this study as a method of :

1. Assessing the statistical significance of the cluster analysis hypotheses.
2. Determining the major source of intergroup differences.
3. Producing a system for catagorizing unclassified samples.

The model used in discriminant analysis is the linear combination

$$Yk = \sum_{j=1}^{p} Ljk\, X\, j + ek$$

where Yk is the discriminant value for the group k ; Ljk are the determined coefficients for Xj variates when j ranges from I to p ; and ek is the error term for group k. The model is discussed by Kendall (1966). The general concept of the method is to subdivide the total dispersion (variance – covariance) matrix of K groups into a between groups and within group source of variation similar to that used in a one way analysis of variance. Discriminant analysis then maximizes the between groups mean variance to the within group mean variance ratio; eg for two groups.

$$Ljk = Ajk - 1\ (X_1j - X_2j)$$

Lj,k is the Mahalanobis distance (the D^2 statistic); Ajk – 1 is the inverse of the weighted within group dispersion matrix and ($X_1j - X_2j$) is the difference between variable j means for groups 1 and 2. The one discriminant function for 2 groups is a line joining the

group means.For more than 2 groups an additional function,orthogonal to the first,is required. (ie the number of functions is (k − 1) (Volland and Connelly, 1978)). Data should be transformed to approximate normality prior to analysis.The use of a stepwise discriminant analysis allows a sequential addition of variables,with the best discriminator being added to the equation first,until all variables contributing to the discriminating "power" are entered. (Berg, 1980; Klecka, 1975). This step−wise analysis also provides an F statistic for evaluating at which step ancillary variables enter the function.

Discriminant function importance can be judged from two measurements ,namely the function eigenvalue,and the associated canonical correlation. The eigenvalue is a measure of the total variance existing in the discriminatory variables,and can thus be used to calculate the total discriminating power (TDP) (Tatsnoka, 1969) as a measure of function variability attributable to group differences.The canonical correlation describes how closely the function and the "group variable" are related.The square of canonical correlation gives the proportion of the discriminant function variance that is explained by the groups,with the significance of the function being measured by the Chi−square statistic (Rao, 1952).

The function,because it indicates probable group membership,can be used for prediction of the membership of unclassified samples (Kerlinger and Pedhager, 1975). Classification functions for each proup are derived from pooled within−groups covariance matrix and centroids of discriminating variables. The classification equation for a group is

$$Ci = Ci_2V1 + Ci_2V2 + \ldots + CipVp + Ci_0$$

where Ci is the classification score for group i;the cij's are the classification coefficients with Ci_0 being the constant,and V's are the raw scores of the discriminating variables. The individual would be classified ,based on the separate group equations, into the group with the highest score. (Keckla, 1975).

5.4.3 Factor Analysis

Factor analysis or, more correctly, principal components analysis is a procedure used to interpret relationships within the variance − covariance matrix of a standardised multivariate data set (Davis, 1973) . Rummell (1967) describes factor analysis as taking

numerous measurements and resolving them into distinct patterns of occurrance , with no particular assumption of underlying variable structure being required. Principal Components Analysis can be separated into two steps.

1. Computation of a correlation matrix of variables as a measure of associations.
2. Extraction of initial components from the correlation matrix as eigenvalues and eigenvectors, with these components being orthogonal or independent of each other (Kim, 1975).

The first of these composite variables or components repres ents the linear combination of variables accounting for more of the variance within the data set than any other combination. The second component is defined as the second linear combination of variables, conditionally orthogonal to the first, accounting for most residual variance in the data following removal of the first component. Subsequent components are defined similarly until all variance in the data is exhausted (Kim, 1975).

The Principal Components Analysis program was used to determine the interrelationships present among chemical, textural and geochemical variables of the soil parent materials, and among geochemical variables alone for both parent materials and clay mineral separates. The variables were standardised prior to analysis so that each variable had a mean of zero and unit variance. This allows comparison between variables when units of measurement differ in type or relative order of magnitude (Davis, 1973).

5.4.4 Trend Surface Analysis.

Trend surface analysis was utilised to analyse the regional trend in compositional variation of the variables indicated to be major sources of variance by factor analysis. This method,in conjunction with routine isopach mapping,illustrates regional variation. Interpretation of the regional trends makes it possible to suggest genetic reasons for the observed variation.

The purpose of trend surface analysis is to detect both the amount and direction of any trend in data values (Doornkamp and King, 1971). Trend surface analysis assumes that a mapped variable can be decomposed into two components that arise from two scales of process:

1. a large scale process that generates a trend component operating over a large area;

2. a local component,or residual,which can be defined as apparently non-systematic fluctations that are superimposed on the large scale patterns (Krumbein and Graybill, 1965).

Unwin (1975) outlines the basic equation for trend analysis as

$$Zobsi = f (xi , yi) + ui$$

where Zobsi is the observed value of the surface at the ith point, xi and yi are coordinates, and ui is the residual. f (xi , yi) denotes the trend surface. The constants for the trend surface are chosen according to the least squares criterion of goodness of fit (Unwin, 1975). The percentage reduction in sum of squares achieved is used to denote the goodness of fit of the calculated surface. The trend surface calculated to describe regional trend most accurately may be linear, quadratic or cubic; higher orders are theoretically possible but are found to generally not improve the fit of the surface. Analyses of residuals from these calculated surfaces are not discussed in this thesis.

The analyses described here, along with other more routine statistical calculations, were performed with the Amdahl 470V/8 at the University of Alberta. The programs utilised are available in the statistical packages described by Nie *et al* (1975) (SPSS), Dixon *et al* (BMDP) (1979), and Wishart (1978) (CLUSTAN). The contour maps, block diagrams and trend surface analyses describing the chemical and textural variations were computed using the SURFACE II package (Sampson, (1978).

6. REGIONAL PARENT MATERIAL CHEMICAL CHARACTERISTICS:

6.1 PARENT MATERIAL CHEMICAL COMPOSITION

The chemical composition of parent material samples from the study region was determined by ICP–AES and AAS after dissolution of the samples with HF and HCl (Appendix VII). The analyses of samples from 94 sites for 18 elements are described in Appendix I, with four extra elements being determined for 46 of these sites. The sample numbers listed will be used as site descriptors for the balance of this thesis, and they can be geographically located on the sample map (Figure 3).This section of the thesis will be subdivided into subsections to address the following objectives:

1. To describe amounts and distribution of the various elements within the study region, and to compare these levels with those described in other studies of Canadian soils.
2. To relate the compositional variations to the textural variations of the soils of the study region.
3. To investigate the utility of multivariate statistical procedures for the differentiation of the major soil parent materials of the region, and for the calculation of classification functions which could be used to describe unit membership of unclassified samples.

The third objective outlined above is considered pertinent to the study because such regional surveys inevitably produce large amounts of data and can only be analysed by application of data reduction techniques. These techniques enable any variable interrelationships to be described and, thus, analysed.

The summary statistics listed in Appendix I indicate that all of the analyzed elements display some deviation from statistical normality. Those elements with skewness values greater than ±0.75 were subjected to a log–normal transformation and all the calculations described in the body of this thesis were repeated using the transformed data as input. As the results did not substantially change any of interpretations based on the standardised data it is these standardised–data based calculations which are described in this thesis. The variability in the textures of the analysed samples is thought to balance the usual log–normal distribution of minor and

trace elements in minerals in natural systems. This may also be a reflection of the presence of igneous, metamorphic and authigenic minerals in these sediments.

6.2 COMPARISON WITH OTHER STUDIES OF CANADIAN SOILS

Mean values for the individual elements (Table 2) are compared with those presented by McKeague *et al* (1979) for Canadian soils, for samples from the Interior Plains, and with the data of Dudas and Pawluk (1980) for tills of Central and Southern Alberta. The data of Shacklette *et al* (1971) for mean concentrations of soil materials from the conterminous United States are also listed for comparative purposes.

The samples analysed in this study also represent a range of textural variation related to the mode of deposition, thus the total sample set was partitioned into subsets based on textural parameters. Accordingly, data for samples with more than 30% clay (N=34), 50% sand (N=30) and 30% silt (N=49) are defined in Table 2 for comparative purposes. The following discussion of elemental composition is based primarily on the mean data from this study as it compares with that of McKeague *et al* (1979).

6.2.1 Minor Elements

The overall mean level of Cu (16 ug gm^{-1}) is lower than that reported by any of the other reseachers whose data is listed in Table 2, but it is close to that described by McKeague *et al* (1979) for samples from the Canadian Shield. The mean levels of Cu in rocks of the Canadian Shield has been described as 14 ug gm^{-1} (Shaw *et al*, 1967, 1975), and in materials of the North East of Alberta as 20 ug gm^{-1} (Pawluk and Bayrock, 1967). The levels in those samples high in clay and/or silt are almost identical to those of the other authors, indicating the importance of secondary minerals as 'concentrators' or 'scavangers' of minor elements. The samples high in silt are also high in clay which may explain the similarity in composition of these two groups. Samples with high sand content have low Cu levels (7 ug gm^{-1}), probably because of the dominance of quartz in these samples. This relationship of minor elements with textural variation has been described by McKeague *et al* (1979), Mills and Zwarich (1975) and Frank *et al* (1976). The levels for the sand fractions (6 ug gm^{-1}) of the soils examined by Dudas and Pawluk (1980) were very close to those obtained for the coarse textured soil materials in this

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Table 2: Mean chemical composition of soil parent materials in the study region. Comparative data are listed from pertinent studies in North America.

Major (%)	Region mean	Clay 30%	Sand 50%	Silt 30%	Shack. N.A.*	Canada McK.**	Interior Plains McK.	Dudas****
Al	4.38	6.06	2.32	5.29	6.6	6.2	5.5	
Ca	1.24	1.36	0.91	1.45	2.4	1.5	2.2	
Fe	2.04	2.79	1.11	2.45	2.5	2.6	2.3	
K	1.14	1.51	0.71	1.37	2.3			
Mg	0.62	0.78	0.36	0.74	0.92	0.82	1.1	
Na	0.4	0.42	0.37	0.45	1.20			
Ti	0.21	0.28	0.12	0.25	0.3	0 44	0.29	
Minor (ug gm)								
Co	14	18	9	17	10	21	18	9.3
Cr	41	61	18	51	53	45	36	
Cu	16	23	7	20	25	22	25	23
Mn	222	254	149	258	560	544	380	
Mo	1.3	1.9	0.6	1.6	2			
Ni	26	37	11	32	20	22	26	
P	458	638	225	581	420			
Pb	16	21	10	19	20	22	17	16
Sr	109	133	79	125	240	207	196	
V	82	131	32	107	70			
Zn	40	58	18	51	54	77	74	59
As *** 5.7						5.2		5.2
Hg ***42						54	89	44
Textural Data (%)								
Clay	25	40	9	32		22	23	29
Silt	29	37	14	39				
Sand	46	23	77	29				

* from Shacklette et al (1971)
** from McKeague et al (1979)
**** from Dudas and Pawluk (1980)

*** Based on 47 samples.

study. Levels for the clay-rich soils (23 ug gm^{-1}) are very close to those described by Lutz and Hendzel (1977) for river sediments in the AOSERP study region.

Cobalt levels are lower than those described by McKeague *et al* (1979), and higher than those described by Dudas and Pawluk (1980) for their study, but are similar to that defined for Shield rocks (12 ug gm^{-1}) by Shaw *et al* (1975). The high clay samples have the same level as that assigned to Interior Plains soils (18 ug gm^{-1}) although the mean clay content of these soils is 17 % higher than that reported by McKeague *et al* (1979), or by Dudas and Pawluk (1980). Cobalt levels in the parent materials of the sandy Brunisolic soils are identical to those reported by Dudas and Pawluk (1980), although their samples contained less than 30 % sand. Their sand fraction analysis documents Co levels 50 % lower than those obtained in this study for materials containing 77 % sand. This suggests that their results may be low, especially as the data of McKeague *et al* (1979) indicate levels almost double for soils of the Plains region. The levels documented in this study are further supported by the data of Shaw *et al* (1975) which show the mean level for Shield rocks to be 21 ug gm^{-1}.

The Cr data show a range from 61 ug gm^{-1} in the high clay soils to 18 ug gm^{-1} in the high sand materials, with the regional mean being 41 ug gm^{-1}. These data are in fairly close agreement with the Canadian (45 ug gm^{-1}) and Interior Plains documented averages (McKeague *et al*, 1979). The data of Shacklette *et al* (1971) for the less than 75 um fraction of subsurface soils of the conterminous U.S.A. (51 ug gm^{-1}) indicate that the levels of this study are about normal background for sediments. River sediments in the AOSERP study area show a mean Cr level of about 85 ug gm^{-1} (Lutz and Hendzel, 1977), but this level is biased by the high clay content of samples from the Athabasca Delta. Mean levels in Shield rocks are 35 ug gm^{-1} (Shaw *et al*, (1975).

The mean regional value for Pb (16 ug gm^{-1}) is identical to that documented by Dudas and Pawluk (1980) and McKeague *et al* (1979) for soils of the Plains region, and recent data indicates the background level for Shield rocks at 17 ug gm^{-1} (Shaw *et al*, 1975). The similarity of levels between the high clay and silt materials, accompanied by only a 6 ug gm^{-1} drop with a 30 % increase in mean sand content suggests that lead is not preferentially enriched in any of the size separates. This may be because of substitution for Ca and K in feldspars and micas. The mean soil levels are double those (8 ug gm^{-1})

reported for sediments in the study region (Lutz and Hendzel, 1977).

Zn data are generally lower in this study, although the high clay samples exhibit levels identical to those obtained by Dudas and Pawluk (1980) who suggested that this element may be found in the octahedral layers of the micaceous minerals substituting for Fe^{++}. The increase from 18 ug gm^{-1} in sand rich to 58 ug gm^{-1} in clay rich samples tends to confirm the above suggestion, especially as less than 2 % ferromagnesian minerals were found in the sand fractions of these samples. McKeague *et al* (1979), with levels 50% above those found either in this study or in that documented by Shacklette *et al* (1971), may have overestimated the Zn levels of Canadian Soils, especially as the background levels for Shield rocks are 52 ug gm^{-1} (Shaw *et al*, 1975). This suggestion is further supported by the fact that Pawluk and Bayrock (1969) document levels of 40 – 50 ug gm^{-1} for the North East of Alberta, and the data of Lutz and Hendzel (1977) for river sediments (42 ug gm^{-1}) are also similar to the levels obtained in this study.

Mn levels described in this study are lower than those documented elsewhere (McKeague *et al*, 1979; Shacklette *et al*, 1971) for background soil levels, but are close to those of Lutz and Hendzel (1977) for Athbasca River sediments (250 ug gm^{-1}) and to the levels described by Pawluk and Bayrock (1969) for this region. This is the only element to show enrichment in the silt materials. This enrichment is probably due to Mn oxide nodules in the soil fabric. These may have been formed from Mn which has been released during weathering of the ferromagnesian minerals in the solum.

Levels of V in this study are similar to those described by Shacklette *et al* (1971) for 563 samples of U.S. soils, yet higher than that described for Shield rocks (53 ug gm^{-1}) by Shaw *et al* (1975). The levels described by Lutz and Hendzel (1977) for river sediments in the area (54 ug gm^{-1}) are also lower, but Allan and Jackson (1978) present data for the same system listing mean levels as high as 103 ug gm^{-1} which are similar to those from samples in the current study with greater than 30% silt or clay in their matrix.

Ni levels in this region (26 ug gm^{-1}) are identical to those listed for the soils of the Interior Plains, but higher than those for both Canadian and U.S. soils (McKeague *et al*, 1979; Shacklette *et al*, 1971). The levels reported for river sediments of the study region range from 33 ug gm^{-1} (Lutz and Hendzel, 1977) to 17 ug gm^{-1} (Allan and Jackson, 1978), with varying levels being apparent in the sediments of the major tributaries of the

Athabasca River in the region.

Levels of both Mo and P are similar to those documented by Shacklette *et al* (1971), with no comparable data being readily available for Canadian soil parent materials, with the exception of the data of Pawluk and Bayrock (1969) who describe a background level of 1 -2 ug gm^{-1} Mo for Northeastern Alberta.

The Sr levels in this study are lower than those reported in the other studies. The samples of soils with more than 30% clay and/or silt (133 ug gm^{-1} / 125 ug gm^{-1}) have levels approaching that described by McKeague *et al* (1979) for soils from the Interior Plains (196 ug gm^{-1}), whereas soils with high sand contents have only 79 ug gm^{-1} Sr.

The As and Hg data are based on 45 samples only, but agree with data described by Dudas and Pawluk (1980) for tills further south in Alberta. The Hg levels (42 ppb) are only half those ascribed to Interior Plains soils by McKeague *et al* (1979), which suggests either wide regional variation or less definitive analytical techniques. The levels for the regional drainage system obtained by Allan and Jackson (1978) show a range of 30 to 74 ppb,which they suggest is normal geological background levels for the region. As levels ranged from 2.0 to 6.3 ug gm^{-1} for the river sediments in the above study, which is similar to those obtained from soil materials in this thesis (mean = 5.7 ug gm^{-1}). Samples from the Birch Mountains area, however, have higher mean values than elsewhere in the study region (9.3 ug gm^{-1}), with a range of 8 - 12 ug gm^{-1}. These soils have haematite and goethite in the clay fraction, and these minerals were shown to be 5 times enriched in As relative to the soil matrix (Rankin and Childs, 1976).

6.2.2 Major Elements

Fe and Ti levels are similar to those reported for the Interior Plains (McKeague *et al*, 1979) and Northeastern Alberta (Pawluk and Bayrock, 1969).The levels of these elements in the clay and silt rich soils show relationships similar to those listed above for minor elements.Allan and Jackson (1978) describe levels as ranging from 1-3 % in river sediments of the region for Fe, and 0.4 % for Ti.

Na is another element to exhibit highest contents in those soils with high silt levels.This may be possibly due to the higher levels of Na-feldspars described as being present in such fractions by Abder-Ruhman (1980). The levels are, however, lower than

those described by Shaklette *et al* (1971) for U.S. soils.The sediments analysed by Allan and Jackson (1978) show a range from 0.45 % to 0.89 %, which is similar to the ranges of soil parent materials in this study.

Mg (0.62 %) and Ca (1.24 %) levels are lower than those of McKeague et al (1979) for Interior Plains soils (2.2 %).This reflects the fact that only about 25 % of this region has calcarcous parent materials.The Ca data indicate that the high silt soils have the highest Ca levels (1.45 %),which agrees with the findings of Smith (1979) for calcareous Podzolic soils in the Rocky Mountains. The suggestion is that secondary carbonates may be more abundant in the silt and clay fractions of the soils,but further research is required to confirm this.

The data of McKeague *et al* (1979) and Shacklette *et al* (1971) indicate higher levels of Al than those obtained in the regional summmary for this study. The close agreement in Al levels for soils having more than 30 % clay or silt in their matrix (6.06 and 5.29 % Al respectively) indicates that the mean regional levels (4.38 %) reflect the levels of those soil materials with 50 % sand in their matrix (2.32 % Al). The ranges documented in the current study are supported by the data presented for river sediments in this region (5 to 8 % Al) by Allan and Jackson (1978).

The comparison of background levels of various elements with those documented for various North American soils demonstrates that these levels have many similarities. The regional mean data is frequently lower than those documented elsewhere and this has been related to the textural variation of the soil parent materials in the AOSERP study region. These discrepancies serve to demonstrate the problems associated with generalisation of regional base levels for different elements without an adequate map based, or statistically designed, sample data base.

6.2.3 Geochemical and Textural Maps

The geochemical maps presented in this section are essentially summaries of the regional variation to be found in the soil parent materials. These maps, using the criteria defined by Doyle (1977) who suggested that it was necessary to collect only 5 C horizon samples from each parent material or surficial deposit to define a stable map pattern in Central Alberta and Saskatchewan, are considered to be stable representations of the

regional compositional patterns (see Figures 4 to 25). These maps, it must be emphasised, are intended to describe only the regional variation, and not the local or within map unit variation. The map data-base is derived from analysis of representative samples collected during a regional soil survey (Turchenek and Lindsay, 1981), and can thus be expected to define the variability of the parent materials at a scale similar to that presented in their report, although the maps presented in this thesis are, of necessity, at a much smaller scale.

These maps were produced using the SURFACE II Graphics System (Sampson, 1978). The isopach maps are generated using a smoothing alogarithm, therefore the lack of data control points along the map boundaries inevitably produces some distortion. This distortion, however, does not alter the regional variation illustrated by the individual chemical or textural parameters.

Examination of the regional maps (Figures 4 to 25) indicates that the regional chemical variation tends to reflect the textural variation, with the higher clay content of the parent materials being in the same part of the study region as the higher mapped levels for various elements. Thus clay, Al, Co, Cr, Cu, Fe, K, Mn, Ni, P, Pb, Sr, Ti, V and Zn tend to be highest in the Birch Mountain region to the north-west of the study region and lowest in the north-east on the Embarras Plain, a region comprised primarily of quartzose sands of glaciofluvial origin. The reverse relationship exists between the sand and elemental levels.

The regional textural variation is illustrated by a sequence of block diagrams, and an example of the relationship between these parameters and the minor elements is depicted by the block diagram showing the regional variation in Cu levels (Figures 26 and 27). These diagrams represent the study region viewed from an azimuth of 45° from the N-S axis, an elevation of 30° above the horizontal plane and at a distance of 10,000 map units (ie. units of the X and Y axes) from the map centre.

The significance of the regional variation illustrated by the geochemical maps was examined by trend surface analysis. The first order and cubic trend surfaces for Cu and Cr are illustrated as examples in Figures 28 to 31. The significance of these surfaces are described in Table 3. The trend surface analyses for this region indicated significant regional variation at the 95 % confidence level.

Table 3: Examples of the statistical descriptions of the regional linear trend surfaces defined by the contour maps in this study.

	ELEMENT	
	Chromium	Copper
Sum squares total	47676.75	7342.94
Sum squares regression	14290.18	1927.16
Sum squares deviation	33386.57	5415.78
Mean squares regression	7145.09	963.58
Mean squares deviation	366.88	59.51
Goodness of fit	0.30	0.26
Multiple correlation	0.55	0.51
F test	19.47	16.19
First degree freedom	2	2
Second degree freedom	91	91
	Solution to Equation	
	69.02	26.48
	-1.65	-0.61
	-0.09	-0.03

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6.2.4 Chemical and Textural Correlations

The relationships between the chemical compositional and textural variables of the soil parent materials is illustrated by means of a correlation matrix (Table 4), with a value of r greater than 0.27 being significant at the 0.01 level for 1 and 93 degrees of freedom (Steele and Torrie, 1980). The values for As and Hg in this table are based on 45 analyses only. All the minor elements show a high correlation with clay content (0.65 or higher), with the exception of Co and Pb. In the case of Co a similar observation was made by Pawluk and Bayrock (1969). The general pattern is similar for the relationships between minor element concentrations and silt content, although the values of the correlation coefficients are generally lower. The elements Mn and P are the exceptions to the above general trends, with Mn having an r value of 0.52 with silt content and P a value of 0.71. Their r values with clay content are 0.30 and 0.70 respectively. This indicates a slight enrichment of these elements in the silt fraction of these sediments. These general relationships are similar to those described elsewhere (Taylor, 1965; Dudas and Pawluk, 1980; McKeague and Wolynetz, 1980).

The lower correlation coefficients of Pb and Co indicate that these elements are not enriched in any fraction. The correlation coefficient obtained in this study are generally higher than those described by McKeague *et al* (1979) for the Interior Plains, possibly because the sample density in this study is more concentrated thus enabling a more accurate representation of regional compositional relationships to be obtained.

The relationships between the major elements and the textural parameters are generally similar for Fe, Al, Ti and K, but Na has no significant relationship with clay and a value of only 0.37 for silt, probably indicating an enrichment of sodic feldspars in this fraction (Abder–Ruhman, 1980). Mg is also more highly correlated with the silt content of the parent material samples (r = 0.53) indicating a possible enrichment of ferromagnesian minerals in this fraction. Ca, on the other hand, has no apparent relationship with any textural parameter. This probably reflects the variation in carbonate content in the soil materials, only 27 % of the samples being calcareous. This lack of correlation of Ca content was also noted by McKeague *et al* (1979) and related to interference from $CaCO_3$ enrichment of the soil matrix. Smith (1979) demonstrated that the presence of $CaCO_3$ produced *textural estimates as much as* 40 % in error for sand

Table 4. Correlation matrix of chemical and textural variables in the soil parent materials of the study region.

	CU	CO	CR	PB	ZN	MN	V	SR	MO	P	NA	K	CA	MG	FE	AL	NI	TI	S	SI	CL	AS
CO	0.66																					
CR	0.93	0.67																				
PB	0.81	0.57	0.73																			
ZN	0.91	0.68	0.91	0.65																		
MN	0.44	0.43	0.47	0.29	0.59																	
V	0.91	0.64	0.95	0.71	0.91	0.34																
SR	0.68	0.41	0.68	0.46	0.66	0.39	0.63															
MO	0.70	0.54	0.68	0.62	0.66		0.71	0.35														
P	0.88	0.58	0.88	0.66	0.94	0.54	0.87	0.76	0.61													
NA					0.34	0.54		0.59		0.42												
K	0.87	0.63	0.92	0.64	0.92	0.51	0.88	0.80	0.51	0.92	0.46											
CA								0.28														
MG	0.41		0.37	0.25	0.37	0.29	0.30	0.49		0.46		0.44	0.79									
FE	0.84	0.66	0.92	0.59	0.90	0.64	0.84	0.65	0.53	0.83	0.34	0.88		0.38								
AL	0.90	0.65	0.96	0.66	0.93	0.52	0.91	0.76	0.54	0.89	0.35	0.97		0.42	0.34							
NI	0.85	0.66	0.89	0.66	0.90	0.55	0.82	0.65	0.46	0.84	0.30	0.88		0.42	0.87	0.92						
TI	0.90	0.64	0.92	0.71	0.90	0.53	0.85	0.72	0.59	0.88	0.29	0.89		0.49	0.88	0.92	0.90					
PH								0.38			0.37		0.59	0.49								
S	-0.82	-0.58	-0.84	-0.63	-0.79	-0.47	-0.75	-0.71	-0.45	-0.77		-0.82		-0.54	-0.80	-0.86	-0.79	-0.87				
SI	0.71	0.53	0.70	0.56	0.71	0.52	0.60	0.61	0.37	0.71	0.37	0.74		0.54	0.70	0.73	0.68	0.74	-0.91			
CL	0.78	0.55	0.84	0.60	0.74	0.35	0.76	0.68	0.46	0.69		0.77		0.45	0.76	0.83	0.76	0.84	-0.92	0.69		
AS*	0.74	0.40	0.79	0.53	0.85		0.86		0.77	0.81		0.73	-0.32		0.68	0.65	0.50	0.63	-0.41	0.41	0.31	
HG*	0.73	0.52	0.72	0.49	0.74		0.78		0.68	0.67		0.64			0.63	0.60	0.38	0.51	-0.38	0.38	0.28	0.81

* AS and HG correlations based on analyses of 46 samples only.

****Only correlation coefficients significant at 0.05 listed.

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distribution, 20 % for silt distribution, and 15 % for clay distribution. The relationship between Ca and textural parameters increases for non-calcareous samples, supporting the data of McKeague and Wolynetz (1979) in their examination of Ca / Sr relationships in a series of Canadian soils.

6.2.5 Principal Component Analysis

The interrelationships between minor and major elements indicated by the correlation matrix are probably related to chemical substitution in the various minerals comprising the soil matrix. The examination of these substitutions is considered beyond the scope of this section of the thesis , although they will be examined in detail in the discussion of the clay fraction chemistry and mineralogy. In order to examine the sources of data variation described by the correlation matrix, the matrix was examined by Principal Component Analysis (Harman, 1967; Kaiser, 1970) using the FACTOR program in the SPSS package of statistical programs (Nie *et al*, 1977).The chemical and textural data were analysed using the following analytical schemes:

1. All variables were input simultaneously for analysis.
2. Chemical compositional data only.
3. Minor element compositional data only were analysed.
4. Major element compositional data only were analysed.

The data were standardised prior to analysis to give a mean of zero and a standard deviation of unity.

The initial factor extracted by Principal Component Analysis tends to be a general factor, which means that it loads significantly on every variable. The second factor tends to be bipolar, as do the remaining factors. This makes factor interpretation difficult, especially as every variable tends to be decomposed into positive and negative factors. This means the complexity of each variable is usually greater than 1 (Nie *et al*, 1975). Examination of plots of orthogonal factors generally indicates grouping of the variables in two-dimensional factor space. Rotation of the original axis produces completely different factor loadings. This rotation causes the clustered variables to load heavily on one factor only, thus producing a simplification in the factor structure, and produces factor loadings which are conceptually simpler than those on the unrotated factors. Thus

Varimax rotation was utilised in an attempt to arrive at "Simple Structure" (Harman, 1967).

Examination of the Varimax rotated factor matrix for the initial analysis (Table 5) indicates that some of the minor elements (Cu, Cr, Mn, Mo, Ni, P and V) and major elements (Al, Fe, K and Ti) are strongly related to the clay component of the parent materials, and negatively related to the sand component. The loading of the silt component suggests the above elements are only moderately important in defining the regional variability of this fraction. This component describes 77 % of the variance in the correlation matrix. The second component, describing 14 % of the variance, reflects textural variation only, with positive loadings from silt and clay, and a negative loading from sand demonstrating the inherent autocorrelation of these variables. The third component is weighted significantly by only three variables (Ca, Mg and pH), which indicate that pH accounts for 6 % of the correlation matrix variance, or of the parent material variability of the study region. The final factor is dominated by Na, which may reflect variation in the Na-feldspar content within the parent materials. A more probable explanation of this factor is that it may reflect the occurrence of sodium salts in some of the lacustrine samples. The loading of Mn on this factor may reflect the accumulation of this element as an oxide phase in the soil materials from the Birch Mountain area.

Analysis of the elemental variables only (Table 6) confirms the high degree of interaction between levels of certain of the minor elements (Cu, Cr, Ni, P, V and Zn) with the major elements Al, Fe, K and Ti. The second component, describing 14 % of the variance, is loaded by Na and Mn. The third component is essentially the same as that obtained in the previous analysis, demonstrating the fact that Ca and Mg levels (and thus pH) describe no more than 7 % of the data variance in the region.

Analysis of minor element compositional data only (Table 7) indicates a strong relationship between Cr, Cu, Mo, Pb, V and Zn in the first component which will be associated with clay mineral species variation in a later section. The second component is dominated by Sr and P, and the third by Zn and Mn. The first principal component describes 90 % of the data variance in this analysis, indicating that there is no simple explanation for the variation in minor element concentration levels within the parent materials within this region.

Table 5: Factor matrices calculated for the chemical and textural variables of the study region.

Principal Components Matrix

	Factor 1	Factor 2	Factor 3	Factor 4
Cu	0.94			
Co	0.68			
Cr	0.97			
Pb	0.72			
Zn	0.96			
Mn	0.55			
V	0.91			
Sr	0.76			
Mo	0.61			0.31
P	0.93			
Na			0.73	
K	0.95			
Ca		0.84		
Mg	0.49	0.68		
Fe	0.92			
Al	0.97			
Ni	0.91			
Ti	0.95			
pH		0.70		
S	-0.90			0.35
Si	0.79			
Cl	0.84			
Eigenvalue	13.63	2.42	1.13	0.53
% variance	76.9	13.7	6.4	3.0

Varimax Rotated Matrix

Cu	0.92			
Co	0.64			
Cr	0.90			
Pb	0.74			
Zn	0.88			
Mn				0.53
V	0.94			
Sr	0.53			
Mo	0.79			
P	0.84			
Na				0.90
K	0.78			
Ca			0.92	
Mg			0.84	
Fe	0.76			
Al	0.81			
Ni	0.76			
Ti	0.82			
pH			0.62	
S	-0.61	-0.73		
Si	0.53	0.53		
Cl	0.65	0.66		

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Table 6: Factor matrices calculated for the chemical variables of the study region.

Principal Component Matrix

	Factor 1	Factor 2	Factor 3
Cu	0.95		
Co	0.68		
Cr	0.97		
Pb	0.72		
Zn	0.96		
Mn	0.55		
V	0.92		
Sr	0.75		
Mo	0.63		
P	0.94		
Na			0.68
K	0.96		
Ca		0.83	
Mg		0.77	
Fe	0.92		
Al	0.97		
Ni	0.91		
Ti	0.95		
Eigenvalue	11.55	1.87	0.99
% variance	80.2	13.0	6.9

Varimax Rotated Matrix

Cu	0.94		
Co	0.67		
Cr	0.96		
Pb	0.76		
Zn	0.90		
Mn		0.56	
V	0.96		
Sr	0.55	0.53	
Mo	0.73		
P	0.83		
Na		0.87	
K	0.83		
Ca			0.87
Mg			0.93
Fe	0.83		
Al	0.89		
Ni	0.83		
Ti	0.88		

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Table 7: Factor matrices calculated for the minor element compositional variables of the study region.

	Principal Component Matrix		
	Factor 1	Factor 2	Factor 3
Cu	0.96		
Co	0.70		
Cr	0.97		
Pb	0.75		
Zn	0.97		
Mn	0.53	0.48	-0.30
V	0.94		
Sr	0.70		
Mo	0.69		
P	0.94		
Ni	0.90		
Eigenvalue	7.67	0.62	0.32
% variance	89.1	7.2	3.7

	Varimax	Rotated	Matrix
Cu	0.72	0.58	
Co	0.58		
Cr	0.68	0.59	
Pb	0.69		
Zn	0.60	0.57	0.52
Mn			0.71
V	0.74	0.59	
Sr		0.71	
Mo	0.77		
P		0.72	
Ni		0.58	0.53

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The analysis of major elements only is, however, simpler to interpret (Table 8). The first component, with high loadings by Al, Fe, K and Ti reflects variation in clay mineral species composition of the materials. The loading of the second component by Ca and Mg can be ascribed to variation in carbonate content (and thus pH). The loading of the third component by Na indicates that 25 % of the variability in major element levels within the soil parent materials can be ascribed to variation in either feldspar composition or salinity of the materials.

The above analyses of the initial correlation matrix indicate that the variability in the parent material chemistry within the study region is related primarily to textural variation, with the actual mineralogical variation within the clay fraction being implicated in minor element variation within these materials. This variation will be analysed in more detail in a later section. The variation in carbonate levels was shown to account for a lesser amount of the regional compositional variation, with either salinity or feldspar species variation being also of minor importance.

6.3 REGRESSION ANALYSES

Both the correlation matrix described above (Table 4), and the Principal Component Analyse (Tables 5 to 7) based on this matrix indicate a high degree of interrelationship between the minor and major element levels present in the materials under examination. Although these relationships can be explained by general geochemical principles using the ionic substitution data described by Pauling (1966), and applied to mineralogical compositions by Goldschmidt (1954), the question to be asked is whether the major element content can be used as a predictor of minor element abundance in these sediments. One approach to answering this question is to use stepwise multiple regression analyses,with the individual minor elements being the dependent variables, and the highly correlated major elements being input as independent variables. The relationship of the clay content of the parent materials to these elements (Al, Fe, K and Ti) indicated that this variable may also be an important predictor of minor element content. This approach was also applied by McKeague *et al*, 1979 with varying levels of success to their data from a range of Canadian soils. This thesis limits addition of independent variables by stepwise regression to those which have an F value for addition to the

Table 8: Factor matrices calculated for the major elemental levels of the soil parent materials of the four major Soil Units of the study region.

Principal Component Matrix

	Factor 1	Factor 2	Factor 3
Na			0.54
K	0.94		
Ca		0.92	
Mg		0.95	
Fe	0.88		
Al	0.99		
Ti	0.83		
Eigenvalue	3.42	1.76	0.33
% variance	62.0	32.0	6.0

Varimax Rotated Matrix

Na			0.54
K	0.94		
Ca		0.92	
Mg			
Fe	0.87		
Al	0.99		
Ti	0.83		

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regression equation of greater than 2.45. Mg and Ca were not generally included as possible independent variables as the presence of secondary carbonates in some of the parent materials would probably lower their utility as predictor elements. The results of the regressions for minor elements are discussed briefly below.

6.3.1 Arsenic

This regresion is based on only 45 samples and, because of the construction of the data matrix, only the major elements Al, Fe, K and Ti were included in the analysis. The equation is given as :

$$As\ (ug\ gm^{-1}) = 6.36\ K\ \% + 1.38\ Fe\ \% - 1.78\ Ti\ \% - 4.32$$

This equation describes 72 % of the variance in the As data within the parent materials of the study region. A plot of standardised residuals with standardised dependent variables indicates a slight curvilinearity which could be removed by either addition of polynomial terms to the regression equation, or a transformation of the As values (Nie *et al*, 1975).

6.3.2 Chromium

Stepwise linear regression accounted for more than 94 % of the Cr variance in the 94 parent material samples from the study region:

$$Cr\ (ug\ gm^{-1}) = 11.08\ Al\ \% + 56.24\ Ti\ \% - 10.37\ K\ \% - 7.57$$

This compares with equations described by McKeague *et al* (1979) which explain a maximum of 84 % of Cr variance using clay and Al as predictor variables in C horizons of Canadian soils. The higher predictability of the equation in the current study is probably related to the regional sampling pattern, whereas that of McKeague *et al* (1979) is based on a few samples of a wide range of provenance lithologies. The equations do, however, confirm the possibility of gaining a reliable estimate of Cr levels based on levels of more easily determined major elements only.

6.3.3 Cobalt

The correlations of Co with the major elements and texture are not as high as those of Cr. Thus the predictive equation below does not explain as much of the Co variance (45 %):

$$Co\ (ug\ gm^{-1}) = 3.75\ Fe\ \% + 27.03\ Ti\ \% + 0.63$$

The equation of McKeague *et al*, (1979) also included Mn and Ni as predictor variables, but these were not included in the analytical scheme of the present study as the objective here is to ascertain the utility of the major element content as a predictor of minor element levels in soil materials of the region. The equation of McKeague *et al* (1979) explained 70 % of the Co variance in their Plains samples, but an equation with Fe and clay as predictors described only 63 % of Co variability in C horizons. Examination of the residual plots indicates a slight curvilinearity which may be corrected by the addition of polynomial terms to the equation, or by transformation of the Co values (Nie *et al*, 1975).

6.3.4 Copper

Although the predictive equation for Cu describes 84 % of the regional variability, the specified variables Cl and K were not included in the regression equation as they did not describe the required 2 % of the residual variability of the element. The equation is:

$$Cu\ (ug\ gm^{-1}) = 2.18\ Al\ \% + 45.99\ Ti\ \% - 3.17$$

Examination of residuals from this equation indicates that the Cu relationships are free from abnormalities, which means that the error components have a mean near zero, are independent and have similar variance throughout the range of Cu values. This equation is different from that of McKeague *et al* (1979) who listed both clay and Al in their equation; they do not include Ti in their calculations. Mg was found to be an important predictor in their regional breakdown, and thus Mg was substituted for Ti in the analytical array to produce the following equation:

$$Cu\ (ug\ gm^{-1}) = 3.84\ Al\ \% + 0.06\ Clay\ \% + 0.71\ Mg\ \% - 0.45\ Fe\ \% - 1.65$$

This equation does not explain as much of the Cu variability (81 %) as the initial one . In both equations Al accounts for 80 % of the described Cu variability, which is not entirely expected as Cu is closer in size to Mg^{++} than Al^{+++} and thus would be expected to proxy for Mg^{++} in mineral structures. An explanation may be that Al^{+++} is associated with Mg^{++} in the octahedra of silicate mineral structures.

6.3.5 Lead

McKeague *et al*, 1979 found that they were only able to explain 30 % of the Pb variability for most sample groups, and 50 % for the Interior Plains samples based on Fe and Mg contents. This prediction difficulty is related to the properties of this element which, in the Pb^{++} valence state, has a similar ionic size to Ca^{++} and K^{+} and may be present in minerals such as feldspars and micas. Taylor (1965) describes evidence which suggests that Pb^{++} does not proxy for the above elements, but occurs primarily as minor sulphide inclusions in feldspar minerals. The equation obtained in this study also describes only 51 % of the Pb variation.

$$Pb\ (ug\ gm^{-1}) = 68.60\ Ti\ \% + 1.71$$

Ti, being the sole predictor of Pb variability, suggests that Pb may be present in the heavy mineral fraction, although data obtained in this study indicates mean levels of 46 ug gm^{-1} in the clay fraction of selected samples. Analysis of the data set replacing Ti with Mg in the array produced the following equation which explains 45 % of the data variability :

$$Pb\ (ug\ gm^{-1}) = 3.38\ Al\ \% - 2.28\ Fe\ \% + 0.09\ Cl\ \% - 1.03\ Mg\ \% + 4.42$$

This equation suggests that much of the Pb may be in occluded form substituting for Al in the octahedral layers of the clay minerals, probably in the micas. The presence of Fe in the equation also indicates that some of the Pb may be in the secondary iron minerals detected in the clay fraction (goethite and haematite). The selection of Ti in the original

equation does not preclude this, as it has been described as a significant component of these minerals (Fordham and Norrish, 1979).

6.3.6 Manganese

The feasibility of predicting the level of Mn from compositional data was much higher in this study (52 % of the variability) than that of McKeague *et al*. (1979) who were able to explain only 5 % of the Mn variability in their Interior Plains data set. The equation is:

$$Mn\ (ug\ gm^{-1}) = 190.5\ Fe\ \% - 111.98\ Al\ \% + 166.19\ K\ \% + 513.02\ Ti\ \% + 24.59$$

However the curvilinear nature of the standardised residual plot indicates need for either polynomial terms in the regression equation, or transformation of the Mn values. The low level of predictability is probably because Mn does not proxy for other elements because of its large ionic size (Mn^{++} 0.91 A°, Mn^{+++} 0.70 A°). Mn is also concentrated in the weathering products of the soil system, and the distribution of these appears to be somewhat random in the samples within the study region.

6.3.7 Mercury

Only two independent variables were selected to describe 54 % of the Hg variation from 41 sites:

$$Hg\ (ppb) = 11.48\ Fe\ \% + 22.68\ K\ \% - 12.95$$

Dudas and Pawluk (1976) found clay separates from parent materials to contain up to 110 ppb Hg and suggested that only some of this is in occluded form in the mineral structure, with the balance being present as organo-mercurials. This would explain the low predictability of the above equation. The selection of Fe and K in this equation indicates that the bulk of the Hg in mineral occluded form is to be found in the micaceous minerals.

6.3.8 Molybdenum

This element is related most highly to Ti in the correlation matrix (Table 4), and thus this element explains 35 % of the variability described by the equation:

$$Mo\ (ug\ gm^{-1}) = 8.76\ Ti\ \% - 0.61$$

The residual plots for Mo display the same data transformation requirements as suggested above for Mn.

6.3.9 Nickel

The equation shown below for Ni describes 87 % of the variability in the parent material samples, compared with the 62 % explanation of McKeague *et al* (1979):

$$Ni\ (ug\ gm^{-1}) = 5.03\ Al\ \% + 65.32\ Ti\ \% - 0.12\ Clay\ \% - 6.78$$

The residual plots reveal that there are no violations of the basic assumptions for multiple linear regression for this relationship.

6.3.10 Phosphorus

The equation described for P explains 87 % of the variability in this element.

$$P\ (ug\ gm^{-1}) = 353.58\ K\ \% + 1250.3\ Ti\ \% - 3.1\ Clay\ \% - 133.02$$

The importance of K in this equation in describing P variability (83 %) suggests that much of the P in these soils may be in the micaceous and feldspar minerals, although electron micrographs of apatite crystals were obtained during the course of this study. A secondary apatite-like mineral was also observed on the surface of weathered calcium feldspars (Plate 1). This secondary Ca-phosphate was also observed forming around root remains which suggests that root exudation may be important in its formation. This phenomenon has been observed in studies of rice roots (Chen *et al*, 1980).

Plate 1: Scanning electron micrographs of phosphorous-rich minerals from the Kinosis Soil Unit.

A, B: Energy dispersive spectrum and micrograph of pyramidal apatite crystals.

C, D: Energy dispersive spectrum and micrograph of secondary minerals with the composition of apatite precipitated on the surface of a quartz grain. The strong Si peak in the spectrum is from the quartz grain.

E: "Apatite-like" mineral precipatated on the surface of an anorthite grain.

F: Crystals of "apatite-like" minerals precipated on the surface of a quartz grain. The secondary mineral grains appear to have formed around a fine root.

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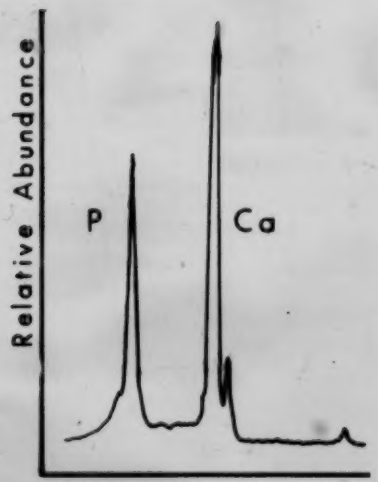

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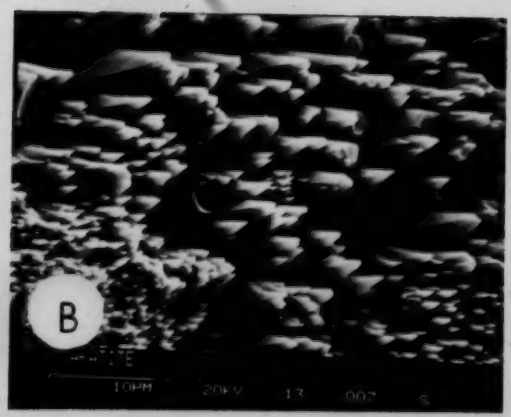

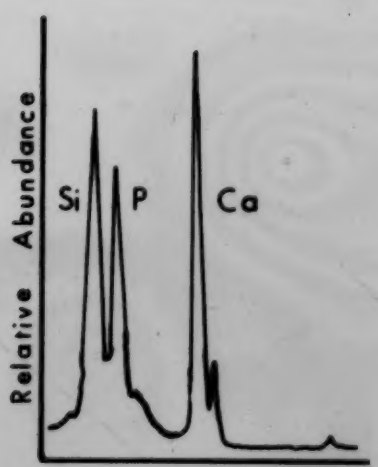

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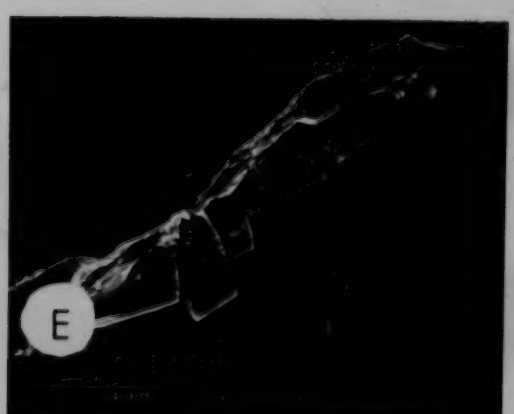

6.3.11 Strontium

Ca and Mg from carbonate rich samples were found by McKeague *et al* (1979a, 1979b, 1980) to affect the prediction of Sr levels. The size of Sr indicates that it may proxy for Ca in silicate minerals and the Ca from the carbonates may mask this relationship. Taylor (1965) states that Sr may also be present in 12-fold co-ordination in micas, where it replaces the K ions. The following equation indicates that this may be the case in the soils of this study:

$$Sr\ (ug\ gm^{-1}) = 74.14\ K\ \% - 12.66\ Fe\ \% + 0.53\ Clay\ \% + 36.95$$

Residual analysis indicates that this equation is valid. A second equation, based on non-calcareous samples (less than 1 % Ca), indicates that Ca only explains 3 % of the Sr variability, whereas K explains 74 %:

$$Sr\ (ug\ gm^{-1}) = 58.65\ K\ \% + 1.02\ Clay\ \% + 15.66\ Fe\ \% + 32.81\ Ca\ \% + 32.18$$

This equation, based on 60 samples, explains 81 % of the Sr variability, whereas the initial equation explains 70 %. Residual plots of this second equation indicate that Sr data transformation, perhaps a log normal as employed by McKeague *et al* (1979a, b), may improve the regression results.

6.3.12 Titanium

Although Ti is generally considered a major element, and has been used in this section as such, the repeated occurrence in the regression equations was unexpected. Thus an analysis was completed to ascertain the relationship of Ti with the other major elements. The equation

$$Ti\ (\%) = 0.04\ Al\ (\%) + 0.03\ Mg\ (\%) + 0.03$$

explains 87 % of the Ti variability. Inclusion of sand and clay levels to the analytical array only improved the predictability another 1 %, thus not providing any insight into the

textural location of the Ti variability. Al describes 86 % of the above 87 % variation indicating that the Ti must be substituting for Al in octahedral co-ordination in the mineral lattices. This implies that the inclusion of Ti in the other equations described in this section may reflect substition in lattices by the individual minor elements in similar positions.

6.3.13 Vanadium

The equation

$$V\ (ug\ gm^{-1}) = 27.02\ Al\ \% - 35.38$$

explains 82 % of the V variability in the samples, and residual analysis indicates that the analysis is correct. The fact that Al explains the V variability was not expected as V is thought to substitute for Fe^{++} and Fe^{+++} in silicate minerals, such as pyroxenes, amphiboles and biotites. The relationship may reflect the substitution by V in the octahedral layers of the secondary phyllosilicate minerals, after having weathered from ferromagnesian minerals (LeRiche and Weir, 1963). V has also been shown to concentrate in iron oxides (haematite and goethite) weathering from ferromagnesian minerals (Taylor and Giles, 1970).

6.3.14 Zinc

The equation computed for Zn explains 90 % of the variability of this element:

$$Zn\ (ug\ gm^{-1}) = 3.0\ Al\ \% + 98.3\ Ti\ \% - 0.3\ Cl\ \% + 5.9\ Fe\ \% + 13.3\ K\ \% - 14.7$$

Residual analysis indicates that the regression is free from any abnormalities. Al describes 87 % of the variability indicating substitution by Zn in the octahedral layer of the phyllosilicate minerals. The inclusion of terms for Ti, Fe and K indicate that the Zn is probably sesquestered in the micaceous minerals, which will be shown in a subsequent section to vary in absolute levels in the major parent materials of the study region.

6.3.15 Conclusion

Stepwise multiple linear regression analyses for predicting minor element concentrations show a high level of explanation for several elements (As, Cr, Cu, Ni, P, Sr and V) when based on major element compositional data for Al, Fe, Ca and Ti, and textural data . Equations such as these could be useful for estimation of concentrations of minor elements in samples from the Interior Plains analysed by techniques such as the Electron Microprobe or X-ray Fluorescence where minor element estimation requires long count times and are generally uneconomic for routine trace analyses. For samples which have been dissolved, however, their use is limited as it is relatively simple to analyse for extra elements by Atomic Absorption or Inductively-Coupled Plasma Spectroscopy, although interference problems with A.A. do definitely effect analytical accuracy. In this case these equations could be used to check the range of the measured values. The applicability of these equations could also be tested by applying them to large data sets such as those listed by Pawluk and Bayrock (1969).

The initial independent variable in the above equations explains 90 % or more of the described variability of the dependent variable. Thus these equations also indicate where the minor elements may be substituted in the lattices of the silicate minerals, and the probability of such substitutions generally fits the geochemical information described by Goldschmidt (1954). This substitution is also suggested by the values in the correlation matrix, and by the Principal Component Analysis described above. However the Principal Component Analysis does not actually define the individual minor element relationships with the major elements because of the large number of strong positive correlations in the initial matrix.

6.4 CHEMISTRY OF INDIVIDUAL SOIL UNITS

The elemental composition data obtained in this study can be broadly divided into two catagories:

1. The first encompasses the entire data set and was used above to describe regional variation and formulate predictive equations to describe probable minor element levels from textural and major element compositional data.
2. The second comprises the first 46 samples of the data set (Appendix I) which are taken in approximately equal numbers from the four most widespread mineral soil parent material units within the study region, namely the Dover, Kinosis, Horse River and Legend units.

The modal composition of these four units is described in Table 9. The mean levels of the individual elements vary between these units, although the standard deviations indicate overlap in many instances. Thus it is important to determine whether the variation in individual estimates is greater within the individual soil units, or between them. This was accomplished using the ONEWAY program available in the SPSS package of statistical programs (Nie *et al*, 1975). The ANOVA performed by this program indicated that the variation in individual elemental levels between the four groups was significant at the 0.05 level for all elements analysed except for Mn and Na. The elements displaying the highest significant variation between units are As, Cr, Cu, Hg, Sr, V and Zn. (Appendix III) The major elements, although significantly different between the units, all have a lower F ratio than the minor elements which indicates that their variability between the individual units is less than that of the minor elements.

As some of these elemental compositional levels display significant differences between the units the possibility of their utilisation as group differentiators was examined. Thus Duncan's Multiple Range Test (Steele and Torrie, 1980) was applied to the mean compositional levels of the soil units to test for differentiation between the individual groups. The groups which have the same subscript are significantly different at the 0.05 level (Table 9), based on individual elemental levels. The Legend unit is consistently separated from the other three units based on As, Cr, Hg, Mo, Pb, V and Zn. The other units tend to be difficult to separate based on any individual element, although the Kinosis unit is separated from the Legend unit by Cu, Ni, P, Sr, and Ti. The isolation of

Table 9: Modal chemical composition of the parent materials of the major Soil Units in the study region.

	DOVER	KINOSIS	HORSE RIVER	LEGEND	REGION
		Major elements (%)			
Al	5.02 ab	4.16 a	5.36 b	5.81 b	5.08
Ca	1.60 bc	0.93 ab	2.48 c	0.29 a	1.30
Fe	2.19 ab	1.94 a	2.52 bc	2.80 c	2.36
K	1.23 ab	1.04 a	1.37 bc	1.44 c	1.27
Mg	0.81 b	0.50 a	0.86 b	0.52 a	0.67
Na	0.45 a	0.42 a	0.46 a	0.40 a	0.43
P	0.054b	0.036a	0.059 b	0.066b	0.05
Ti	0.27 b	0.21 a	0.26 b	0.27 b	0.25
		Minor Elements (ug / gm)			
As	4.2 ab	3.6 a	5.6 b	8.9 c	5.6
Co	10.0 a	14.0 ab	20.4 bc	22.3 c	16.8
Cr	47.5 ab	37.9 a	50.5 b	65.9 c	50.5
Cu	19.5 b	15.8 a	20.8 bc	23.7 c	19.9
Mn	246 a	230 a	258 a	286 a	255
Mo	1.4 a	1.6 a	1.3 a	3.3 b	1.9
Ni	32.5 b	22.6 a	37.6 b	35.4 b	31.9
Pb	18.0 a	18.4 a	17.5 a	22.7 b	19.2
Sr	137 b	91 a	122 bc	112 c	115
V	88.1 a	66.8 a	97.9 a	150.5 b	101.2
Zn	46.1 ab	37.6 a	50.9 b	63.8 c	49.7
			(ppb)		
Hg	31.8 a	30.3 a	45.7 b	59.7 c	41.6

Elements followed by the same letter are not significantly different at the 0.05 level based on Duncan's New Multiple Range Test.

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these two units will be related to diversity of sediment provenance in more detail in the discussion of clay mineralogy. Here it is sufficient to state that that the unit separation is related to the high proportion of Shield sediments incorporated into into the Kinosis unit, and a correspondingly high proportion of bedrock from the Upper Cretaceous Smokey Group in the Legend unit. The Dover unit reflects a diverse source, with the Shield derived sediments comprising the major source (Christiansen, 1976). The Horse River unit is also similar to the Kinosis unit with the addition of calcareous material from the Devonian outcrops in the north east of the study region (Turchenek and Lindsay, 1981).

Examination of the results of the Duncan's Multiple Range Test indicates that no individual element content is sufficient to separate adjacent map units, and that several are necessary to differentiate the Kinosis and Legend units from the other two. The Dover and Horse River units are not completely isolated by any of the measured variables. The lack of clear distinction between the individual units indicates that the regional variation may be best described by the utilisation of various numerical classification techniques. Application of techniques such as Principal Component Analysis and Discriminant Analysis in soils-related studies have been described in the introductory sections of this thesis.

6.4.1 Principal Component Analysis

Principal Component Analysis was utilised to analyse the interelement relationships in the four parent material units. The data were standardised prior to analysis to give a mean of zero and a standard deviation of unity, a technique which has been successfully applied to soils data by Stynes *et al*, (1979). The FACTOR program in the SPSS statistical package (Nie *et al*, 1975) was utilised. Principal components were extracted, and a Varimax rotation was performed.

The chemical composition data were analysed in three sets:

1. The total compositional data were analysed.
2. The minor elements only were input.
3. The major elements only were input.

The textural variables were excluded from the analytical array because the correlation of these with the chemical data was adequately examined in the discussion of the overall

regional parent material variation.

The results of these analyses are given in Tables 10 to 12. The importance of individual variables (elements) as members of a component are indicated by the magnitude of their loadings, and, as has been mentioned previously, these components are generally interpreted in the earth sciences as factors describing geochemistry, mineralogy, hydrology or provenance.

The initial analysis (Table 10) defined four component to explain the variability of the data matrix, with Component I explaining 71 %, Component II explaining 15 %, Component III explaining 8 % and Component IV explaining 6 % of the variance in the initial correlation matrix respectively. Examination of the resultant Varimax rotated factor matrix, in which a simplified geometric structure is defined, indicates that the first factor, explaining the major proportion of the variance, reflects high loadings by Cr, Cu, P, V and Zn in the minor elements and Al, Fe, K and Ti in the major elements. These elements will be shown in the discussion of clay mineralogy to be associated with the smectite and micaceous minerals, and thus this first factor is related to clay mineralogical variability in the parent materials. The second factor has relatively high loadings by As, Co, Hg and Mo. The latter element was shown in the clay mineralogical analyses to be associated with authigenic smectites, and the linking with As and Hg suggests that these elements may also be enriched in these minerals. This is at variance with the suggestion of Dudas and Pawluk (1980) that As is not uniformly enriched in the clay fraction of Alberta soils. Taylor (1965) states that As is mainly present in the sulphide phase, and the shales of the Smokey Group do contain arsenopyrites which are the probable source of the higher levels obtained in the Legend unit members. Fordham and Norrish (1979) demonstrated that As was retained by goethite, which was observed in diffractograms of clay separates from the region, and Ti oxides. The high correlation coefficients of As, Fe and Ti suggests that this is a more likely possibility in these sediments.

Dudas and Pawluk (1976) presented data showing Hg enrichment of the clay fraction, and stated that the actual mineral occluded Hg may only account for 10 % of the total content. Co was found to be only moderately enriched in the clay fraction of Alberta soils (Dudas and Pawluk, 1980). The initial correlation matrix indicates that these four elements (As, Hg, Co, Mo) are more highly correlated with the silt fraction, thus

Table 10: Factor matrices calculated for the chemical compositional variables of the major Soil Units of the study region.

Principal Component Matrix

	Factor 1	Factor 2	Factor 3	Factor 4
Cu	0.93			
Co				
Cr	0.97			
Pb	0.63			
Zn	0.96			
Mn			-0.49	
V	0.96			
Sr				-0.51
Mo	0.69			
P	0.89			
Na				
K	0.92			
Ca		0.82		
Mg		0.89		
Fe	0.87			
Al	0.92			
Ni	0.73			
Ti	0.84			
Hg	0.77			
As	0.84			
Eigenvalue	10.74	2.33	1.24	0.93
% variance	70.5	15.3	8.2	6.1

Varimax Rotated Matrix

Cu	0.88			
Co		0.51		
Cr	0.91			
Pb	0.51			
Zn	0.88			
Mn				0.62
V	0.84			
Sr	0.51			
Mo		0.64		
P	0.89			
Na				
K	0.94			
Ca			0.97	
Mg			0.90	
Fe	0.85			
Al	0.94			
Ni	0.76			
Ti	0.86			
Hg	0.55	0.69		
As	0.68	0.54		

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Table 11: Factor matrices calculated for the minor element levels of the major Soil Units of the study region.

	Principal Component Matrix		
	Factor 1	Factor 2	Factor 3
Cu	0 92		
Co			
Cr	0.95		
Pb	0.67		
Zn	0.94		
Mn			-0.48
V	0.96		
Sr			0.57
Mo	0.77		
Ni	0.67	0.50	
Hg	0.81		
As	0.88		
Eigenvalue	6.81	0.96	0.84
% variance	79.1	11.1	9.8

	Varimax	Rotated	Matrix
Cu	0.66		0.50
Co	0.51		
Cr	0.66	0.55	
Pb	0.70		
Zn	0.63	0.73	
Mn		0.53	
V	0.75		
Sr			0.74
Mo	0.91		
Ni		0.74	
Hg	0.79		
As	0.80		

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Table 12: Factor matrices calculated for the major elemental composition of the four Soil Units.

	Principal Component Matrix		
	Factor 1	Factor 2	Factor 3
Na			0.54
K	0.94		
Ca		0.92	
Mg		0.95	
Fe	0.87		
Al	0.99		
Ti	0.83		
Eigenvalue	3.42	1.77	0.34
% variance	62.0	32.1	6.0

	Varimax Rotated Matrix		
Na			0.54
K	0.94		
Ca		0.92	
Mg		0.94	
Fe	0.87		
Al	0.99		
Ti	0.83		

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suggesting that this factor may represent some mineralogical variation in the silts, probably related to the incorporation in secondary oxides or sulphides of iron or titanium. The third factor, with high loadings by Ca and Mg, reflects variation in the carbonate content of the parent materials, and thus is related to pH. The highest loading in the fourth factor is by Mn which may be related to the mangans observed in thin section examination of the C-horizon of a Legend unit profile. Mangans have previously been described and analysed in calcareous parent materials in Alberta (Sanborne, 1981), but not in parent materials as acid as those found in this Soil Unit.

Varimax rotation of the principal components of the minor element data only (Table 11) indicates the As, Hg, Mo and V account for the majority of the variance of the data set. These elements have been related to variation of secondary oxide and sulphide content in the previous analysis. Cr, Ni and Zn are most important in the second factor and are probably related to variation in the micaceous mineral content of the parent materials. Sr, which loads heavily on the third factor, may also be linked with micaceous component variation (Taylor, 1965), although it may also be related to variation in the distribution of Ca-feldspars (McKeague and Wolynetz, 1979). Sr has also been shown to substitute for Ca in carbonate minerals.

Analysis of the major elements only also produced three independent principal components (Table 11). The first, reflecting Al, Fe, K and Ti variability, describes 62 % of the data variance. This component is probably related to the variability in total content of micaceous minerals in the parent materials. The second component, describing 32 % of the variance, is again related to the calcareous nature of the materials. The remaining 6 % of the variability is related to the Na variation, which may be related to variation in amounts of feldspar in the units or to the salinity of the soils in the Dover unit.

The application of Principal Component Analysis to the chemical data has indicated that the major proportion of the variance in these data is related to minor element variability within or between the soil units, which, in turn, is related to variability in the clay fraction mineralogy. These analyses, however, give no basis for defining the individual soil unit membership based on the individual sample analyses. The following section will describe the application of Discriminant Analysis to define linear equations which can be used to define the most probable group membership of unknown samples

from within the study region.

6.4.2 Discriminant Analysis

The ANOVA tables (Appendix III) indicate that the trace elements As, Cr, Cu, Hg, Sr, V and Zn have a higher variability between units than within them. These same variables were shown by Duncan's Multiple Range Test (Table 9) to separate at least one unit from the other three in all cases, and Principal Component Analysis demonstrated collectively these elements describe up to 70 % of the variability of the correlation matrix describing the compositional data relationships for the four soil units under study. Although the major elements Al, Fe, K and Ti do display significant differences in mean contents between the soil units the F levels in the ANOVA tables indicates that their discriminatory power would not be as powerful as that of the minor elements. The clay fractions of these units will be shown to reflect diverse provenance of the different parent materials, and the trace element contents of these minerals varies with provenance. Thus the minor elements listed above were used in the calculation of the discriminant functions for unit differentiation.

The DISCRIMINANT routine in the SPSS statistical package (Nie *et al*, 1975) was used to calculate the discriminant functions. An F level of greater than 2.88 was required for inclusion of a chemical variable into the discriminant equation, based on 1 and 23 degrees of freedom at the 0.05 level. The selection criterion used in the calculations was based on the smallest F ratio between the group pairs in order to maximize the Mahalonobis distance between the two groups. The analyses in this section were based on two group examples, as the classification problems for deciding group membership would generally occur in boundary regions. The discussion focuses on standardised discriminant functions as the coefficients reflect the relative importance of the variables in the linear function. The unstandardised classification functions are described in the accompanying table (Table 13).

As the analyses associated with the clay mineralogy reflect the varying provenance of the two major till parent materials, the first discriminant analysis was performed between the Kinosis and Legend soil units. The function listed below has a canonical correlation of 0.87 and a Total Discriminating Power (TDP) of 0.73 (Tatsnoka,

Table 13: Discriminant analyses for differentiation of the four major Soil Units of the study region.

Element	Stand Coeff.	Unstand Coeff.	Group Centroid Kinosis	Group Centroid Legend	Chi sq.	Can. Corr.
Cu	-1.15	-0.26	-1.67	1.67	29.36	0.88
As	1.88	1.01				
Constant		-1.21				

Element	Stand Coeff.	Unstand Coeff.	Group Centroid KIN+HRR	Group Centroid Legend	Chi sq.	Can. Corr.
Cu	-1.78	-0.35				
Cr	1.22	0.08	-0.96	1.84	33.28	0.81
As	1.34	0.68				
Constant		-1.17				

Element	Stand Coeff.	Unstand Coeff.	Group Centroid Kinosis	Group Centroid HRR	Chi sq.	Can. Corr.
Hg	0.52	0.05				
As	0.48	0.33	-1.36	1.48	22.77	0.83
Sr	0.69	0.04				
Constant		-8.14				

Element	Stand Coeff.	Unstand Coeff.	Group Centroid Kinosis	Group Centroid Dover	Chi sq.	Can. Corr.
Sr	1.00	0.05	1.28	-1.17	19.89	0.79
Constant		-6.04				

Element	Stand Coeff.	Unstand Coeff.	Group Centroid Dover	Group Centroid HRR	Chi sq.	Can. Corr.
Hg	1.00	0.09	-0.67	0.67	7.75	-0.57
Constant		-3.71				

Element	Stand Coeff.	Unstand Coeff.	Group Centroid Legend	Group Centroid Dover	Chi sq.	Can. Corr.
As	0.95	0.06				
Sr	-1.62	-0.74	1.64	-1.50	28.49	0.85
Zn	0.68	0.03				
Constant		-2.29				

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1970). This means that 73 % of the variability in discriminant space is relevant to group differentiation.

$$Di = -1.15\ Cu\ (ug\ gm^{-1}) + 1.16\ As\ (ug\ gm^{-1})$$

The inclusion of As in the above equation reflects the higher level of this element in the shale rich Legend unit (8.9 ± 2.3 ug gm^{-1}) as compared to the Kinosis unit (3.6 ± 1.2 ug gm^{-1}). As has been shown to be enriched in shales (Taylor, 1965). The inclusion of Cu in the equation confirms the findings of Potter *et al* (1963) who stated it to be a reliable indicator of sediments of marine provenance, and is also related to the higher levels in the Legend unit. This discriminant function, although only describing 73 % of the data variability, correctly classified all samples of the Kinosis and Legend units.

The clay data indicate that the chemistry of the Kinosis and Horse River units is similar, and thus these units are grouped as one for comparison with the Legend unit. The resulting standardised discriminant function is:

$$Di = 1.22\ Cr\ (ug\ gm^{-1}) + 1.34\ As\ (ug\ gm^{-1}) - 1.78\ Cu\ (ug\ gm^{-1})$$

This function has a canonical correlation of 0.81 and a TDP of 0.64. Application of the classification functions (Table 13) indicated that samples 28 and 39 (both Legend) were misclassified. Because these sites are on the north east fringe of the Birch Mountain upland, they could have a significant proportion of Shield material in their matrix. If so, this would explain their reclassification on the basis of this function. Field classification of sample 27 in the Horse River unit was reclassified on the basis of the function (Table 13), and the physical location of this site near the southeastern limit of the Legend unit explains the field misclassification.

As both As and Hg were not analysed in the clay fraction, the above Discriminant Analysis were repeated without these elements in order to enable comparison of the classification functions based on whole sample analysis to be compared with those based on clay fraction analysis, which will be presented in a subsequent section. The resultant equations (not shown) indicated that V was the most important discriminating element.

Although this agrees with the data of Potter et al. (1963), the classification based on these latter equations correctly groups [redacted] of the samples.

The discriminant functions for combinations of the parent materials are given in Table 13. The most significant discriminating element for combinations of the Legend, Horse River and Dover units was As, with Sr also being included in the case of the Horse River unit. The presence of the Sr, and the Zn in the Dover separation, indicates that the micaceous component of the sediments which are known to be enriched in these two elements may be important for the chemical separation of these units.

The Kinosis / Horse River, and the Kinosis / Dover discriminant analyses indicate the strong provenance similarities of these sediments, as the discriminations are not as good as those obtained with the Legend comparisons. Sr is the most important discriminating variable in both cases, with Hg also being selected in the first and V in the second. One reason for some of the similarities between the Horse River and Dover units is related to the shallowness of the lacustrine deposits in some of the Unit, and to the presence of waterlain till material interspersed with the lacustrine sediments. This means that some of the sites classified as Dover may actually have a II Ck horizon consisting of till or till-like material.

6.4.3 Conclusion.

Application of Discriminant Analysis using the minor elements shown to describe the most variability between the individual soil units produced equations which can be used for group classification. The Legend unit was shown to be chemically distinct from the other three units, with the resultant classification functions being based primarily on As, Cr and Cu. These elements are enriched in marine shales (Potter *et al*, 1963), and their selection as unit discriminators must reflect their enrichment in the sediments of the Smokey Group which are the dominant materials in the matrix of the Legend unit parent material. Discrimination between pairings of the other units (Kinosis, Horse River and Dover) was based on Sr, Hg and V which probably reflects variation in the absolute levels of micaceous minerals in these sediments.

7. MINERALOGY AND COMPOSITIONAL CHEMISTRY OF THE CLAY SEPARATES OF THE MAJOR SOIL UNITS.

7.1 CLAY SEPARATE MINERALOGY.

The mineralogy and chemistry of the clay fraction was examined by X-ray diffraction, total dissolution (Appendices VII and VIII), differential thermal analysis, infrared spectroscopy, cation exchange and surface area characteristics. Positive X-ray identification of the clay mineral components required the use of nine cation / solvation / heat / hydration treatments. X-ray diffraction data were used primarily to provide qualitative species identification on which to base quantitative compositional estimates using guidelines defined by Alexiades and Jackson (1966). The mica and paragonite quantities were based on ideal end-member compositions, with muscovite having a K content of 8.3 % based on the data in Jackson (1973), and paragonite having an Na content of 6.02 %. These assumptions may, however, be an inaccurate estimation as short ranges of solid solution exist up to about 20 mole % Na in muscovite, and 5 mole % K in paragonite (Nicol and Roy, 1965). The corresponding changes in basal spacing are small, with the presence of (060) peaks at 1.486 A^0 and 1.503 - 1.499 A^0 being indicative of paragonite and muscovite respectively.

Smectite content was determined from the potassium exchange capacity (KEC) assuming an average exchange capacity for smectite of 105 me. 100 gm^{-1}. Surface area measurements (after deducting 810 m^2 gm^{-1} for vermiculite and 20 m^2 gm^{-1} for mica) were also used to estimate smectite assuming a surface area of 810 m^2 gm^{-1} (Carter *et al.* 1965). The content of smectite based on surface area was generally slightly higher than that obtained from KEC calculations. This discrepancy could arise from the contribution of amorphous colloids of low measured CEC but high surface area. Also the X-ray characteristics of the soil smectites indicate a poorer degree of crystallinity than that of the geological specimen used as a calibration standard in surface area determinations.

Vermiculite was determined from the difference between CaEC and KEC, with an assumed interlayer exchange capacity of 154 me. 100 gm^{-1} (Coffman and Fanning, 1974).

Relative amounts of kaolinite plus chlorite were estimated quantitatively in the clay fraction by difference from 100 %. The amount of kaolinite in the samples was calculated using the empirical relationship using the intensities of the 3.59 A° and 3.54 A° diffraction peaks (Carver 1971), and the amount of chlorite was then calculated by difference. As the amounts of these two minerals reported in this study were higher than those reported previously in Alberta soil parent materials (Pawluk, 1961;Twardy, 1969; Pawluk and Bayrock, 1969; Dudas and Pawluk, 1970; ; Abder-Ruhman, 1980), the estimates were checked by independent methods of calculation. The equation, based on the method of additions, developed by Ruhe and Olsen (1979, 1980) for Wisconsinan glacial material in Indiana were used to calculate the amounts of kaolinite present in 45 samples. The equation is given as

$$\text{Kaolin \%} = -2.67 + 70.88\ Ki$$

where Ki is the kaolinite intensity ratio calculated from the glycolated X-ray diffraction patterns. The compositional estimates based on this equation were generally within about 5 % of those obtained by difference; this variation approximates the amount of chlorite present in the samples based on visual estimatations of the diffractograms obtained from the 550° C treatment. Comparison of the results from the three methods of estimation of kaolinite are illustrated in the bivariate plots shown in Figure 36. These calculations confirm the estimates of kaolinite content obtained in this study, and the higher levels discovered are probably related to differences in the source lithologies of the bedrock incorporated into the soil parent materials by glacial action in this region.

Differential thermal analysis has also been used for kaolinite quantification based on measurement of the peak area and width of the dehydroxylation endotherm (500° - 600°C) at half maximum, and calculation of the slope ratio (Bramao *et al.*, 1952). The calculation is based on the equation

$$\text{Kaolinite \%} = \frac{(A / W)_{sample} * 100}{(A / W)_{graph}}$$

where (A / W)graph is the value for a 100 % kaolinite sample having the same slope

ratio as the unknown, and is obtained from the linear correlation plot of Carthew (1955). The results shown in Table 14 demonstrate the sometimes poor agreement obtained between this method and the other two. This may be linked to several properties of the parent material clay samples; the degree of crystallinity, the degree of order and variations in particle size (Smykatz-Kloss 1974, 1976).

Minor amounts of quartz and, in some samples, feldspars were evident in the X-ray diffractograms, but semi-quantitive estimates of their contents were not attempted for the general characterisation of the modal clay suite of the major parent materials of the study region. These modal estimates are given in Table 15, and the chemical and physical measurements on which they were based are presented in Appendix II. X-ray diffractograms of individual samples with amounts of individual components approaching the mean values of Table 15 are depicted in Figures 33,34,35,36.

Three of the Soil Units, Dover, Kinosis and Horse River, have similar amounts of micaeous minerals, smectites and kaolinite plus chlorite, whereas the Legend Unit has a higher amount of smectite, and correspondingly lower amounts of kaolinite and chlorite. This difference is demonstrated by the change in the smectite / (Tmica + kaolinite + chlorite) ratio shown in Table 15.

As the mean values of mineralogical compositions appear to differ among the individual units, it beomes necessary to determine whether this apparent variation is greater within the individual units, or between them. This was accomplished using the ONEWAY program available in the SPSS package of statistical programs (Nie *et al*, 1975). In this program, a One Way Analysis of Variance is performed to determine if the analysed variable varies significantly between any of the four units. All mineralogical components were found to vary significantly at the 0.05 level between the four units with the exception of smectite, the levels of which are based on CEC and KEC determinations (Appendix II). The smectite levels based on surface area determinations are, however, significantly different between groups at the 0.05 level.

As some of the mineralogical components differ significantly between the individual units, it should be possible to use this property to differentiate the units. Table 15 shows the mean value for the mineralogical composition of the four units. Duncans

Table 14: Comparison of the estimates of kaolinite content of the bulk clay separates by different methods.

Soil Unit	Kaolinite Content (%)			
	Differential Thermal Analysis	*Calculated by difference (a)	Peak Intensity (b)	Difference (a - b)
Dover	45	35	28	7
Kinosis	29	37	27	10
	35	40	31	9
	32	45	33	12
Legend	32	24	20	2
Horse River	43	30	26	4
	33	20	na	

* (100 -(Smec+Tmica+Kaol+Chl+Verm))
(a - b) = Chlorite (%)

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Table 15: Modal estimates of the mineralogical composition of the clay separates from the major Soil Unit parent materials of the study area.

Mineral	Dover	Kinosis	Horse River	Legend
		(%)		
Paragonite	5.0	3.0 a	4.0 a	3.2 a
Mica	23.0 a	23.0 a	27.0 b	34.4 b
Mica (Total)	28.0 ab	27.0 a	31.0 b	37.5
Vermiculite	8.0 a	6.0 ab	9.0 a	3.0 b
Smectite (KEC)	30.0 a	31.0 a	32.0 a	37.0 a
Smectite (S.A.)	32.0 a	39.0 b	35.0 a	43.0 b
Kaolinite + Chlorite *	35.0 ab	37.0 a	29.0 bc	23.0 c
Chlorite **	10.0 a	13.0 b	8.0 a	4.0 c
Kaolinite **	24.8 a	23.9 a	21.4 a	19.0 b
Smec./(TM+K+Chl)	0.49	0.48	0.53	0.6

Means followed by same letter are not significantly Different at the 0.05 level using Duncan's New Multiple Range Test.

* Calculated by difference

** Calculated using XRD peak intensities (Carver, 1971)

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New Multiple Range test (Steele and Torrie, 1980) was applied to these means, and those which are not significantly different at the 0.05 level have the same subscript. The Legend unit is consistently separated from the other three units. This separation is probably related to the incorporation of material of Cretaceous bedrock origin into the till matrix by glacial action. The other units appear to have a relatively uniform provenance based on the similarities in mineralogical composition.

Oxygen isotopic analyses of the clay separates for selected samples from three of the soil units (Table 16) reflect the mineralogical differences separated by the multiple range test. These isotopic differences are probably related to the formation conditions of the authigenic clay components, namely the smectites and kaolinites (Savin and Epstein, 1970). This has been verified using least squares analysis as outlined by Savin and Epstein (1970) for a range of soil profile clay separates (not presented). Data presented in Table 16 show a wide difference in isotopic signature for the two major till units. The Kinosis unit clay separate analyses (13.9 ± 0.5 $^{0}/_{00}$) are very close to those reported by Hoeve (1981) for mixed kaolinite / illite / chloritic clays from various members of the Athabasca Group to the north east of the study area. This supports the theory of McPherson and Kathol (1977) that Pleistocene ice flow was from northeast to southwest in this region, and thus the sediments of the Kinosis till would be largely composed of material from the Shield region.

Clay separates from the Legend Unit (17.04 ± 0.17 $^{0}/_{00}$), on the other hand, have a signature similar to that reported for clays from Cretaceous sediments of the Fort McMurray region (K. Muelenbachs, pers comm)[1] , of Cretaceous siltstones in southern Alberta (Longstaffe, 1981) and of Cretaceous shales and associated soils in U.S.A. (Savin and Epstein, 1970; Lawrence and Taylor, 1972). Separates from the Dover unit reflect the signature of the Kinosis type clays (14.14 ± 0.25 $^{0}/_{00}$) to the east of the region, supporting the regional deglaciation model of Chritiansen (1979) which postulates water (and sediment) flow through the Clearwater Spillway into Glacial Lake MacConnell at about 10,000 B.P. The sediment source for this spillway would have been primarily from the decaying ice-front to the north-east. The one sample from the Horse River unit (14.34 $^{0}/_{00}$) also reflects a high component of Shield material in the sediments. The increase in

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Table 16: Oxygen-18 enrichment in the bulk clay separates of selected samples from within the major Soil Units of the study region.

SOIL UNIT			
Kinosis	Dover	Horse River	Legend
13.39 *	14.34	14.34	17.17
13.74	14.07		16.85
13.70	14.37		17.09
14.09	13.96		
14.65	13.75		

*Samples from transect from northeast to southwest of this unit.

All values reported as parts per thousand enrichment with O-18 in the bulk clay separates.

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^{18}O content of the Kinosis clays from the northeast to southwest (13.39 to 14.65 $^{o}/_{oo}$) reflects the incorporation of material from the Lower Cretaceous Clearwater and Grand Rapids Formations of the Stoney Mountain Upland (Turchenek and Lindsay, 1981). Mass balance calculations (Lawrence and Taylor, 1980) indicate that the surficial till to the south of the Stoney Mountain Upland is comprised of about 12 % Cretaceous sediments, which does not compare favorably with the estimate for local bedrock in tills (85 %) of East Central Alberta based on heavy mineral composition (Bayrock, 1962). Field mapping in the Stoney Mountain region indicated the presence of a shaley basal till below the surface ablation till. This shale component may be reflected in the higher isotopic signature of the clay separates analysed from this area

Application of the isotopic signatures of clay minerals to provenance studies for marine sediments (Savin and Epstein 1970; Lawrence, 1979; Eslinger and Yeh, 1981), of quartz grain provenance in a range of soils (Syers *et al* ,1969; Jackson *et al* ,1971; Sridhar *et al*., 1975, 1978) and of the source of calcium carbonate grains in various soil horizons (Mararitz and Amiel, 1980; Salomons and Mook, 1976) have been described. However, there has been no application of this technique to ascertain provenance of glacial materials.

The different provenances of two of the major parent material lithologies within the study region meant that detailed clay mineralogical examination of representative samples could be completed to ascertain whether there are any subtle variations in the mineral group compositions which may be related to sediment provenance. Representative clay samples were thus fractionated for more detailed study of individual mineral species.

7.1.1 Fine Clay Fraction:

The diffractograms of the fine clay separates depicted in Figures 37 and 38 are characteristic of the Legend and Kinosis Soil Units.Analysis indicates admixtures of smectite, mica and kaolinite. The 17 A° and 14 A° peaks for glycerol saturated specimens and a 16 – 17 A° peak for etheylene glycol solvated specimens is chacteristic of a mixture of beidellite / vermiculite and montmorillonite (Harward *et al*., 1969).

The nature of the smectite component was further defined using the Greene–Kelly test which some mineralogists believe differentiates smectites with isomorphic substitution mainly in the octahedral layer (montmorillonite) from those with isomorphic substitution mainly in the tetrahedral layer (beidellite, nontronite, saponite) (Ross and Mortland, 1966). This test, which is based on Li^+ saturated specimens, causes octahedrally substituted smectites to remain collapsed at 9.5 A° whereas tetrahedrally substituted smectites expand to 17 A° following glycolation of specimens previously heated to 300° C for six hours. Schultz (1969) found that a broad peak at 14 – 15 A° indicated the presence of approximately 30 % re–expandable layers in beidellitic clays which were subjected to the Greene–Kelley test, whereas 45 % re–expandable layers gave a peak at 18 A° and this shifted to 19 A° as the beidellite component became more dominant. Kodama and Brydon (1965), using the Greene–Kelley test, related the peak about 14 – 15 A° to a mineral intermediate in composition between montmorillonite and beidellite for tills from southern Alberta. This suggestion is also mentioned by Brindley and Brown (1980).

Bystrom–Brusewitz (1975) suggest that the Greene–Kelley test may give anomalous results if the Li reacts with glass slides, but slide inversion as outlined in their report showed this not to be the case. The strong 9.8 A° peak in both patterns indicates that octahedrally substituted smectite (montmorillonite) is the dominant smectite in both Soil Units. The peak in the Kinosis unit at 17 A° is indicative of a significant proportion of tetrahedrally substituted smectite. The broadness of this peak is similar to the "soil beidellite" reflection described by Ross and Mortland (1966). The peak at 14.3 A° in the Legend clays suggests a lesser amount of beidellite. Application of the method outlined by Schultz (1969) utilising the ratio of the 18 A° to 9.6 A° peaks indicates that 48 % of the net layer charge is in the tetrahedral layer for the Kinosis sample (ie 48 ± 5 % of sample is beidellite). No more than 20 % expandable clay is present in the Legend unit.

Diffractograms of K–saturated specimens heated to 105°C and rehydrated to 54 % R.H. indicate only partial rehydration of the collapsed layers based on comparison of the 10 A° and 7 A° peaks to those of the Ca 54 % R.H. pattern. This partial rehydration behaviour supports the presence of both high charge smectites and/or vermiculite, and low charge species of smectite. Both Weaver (1958) and Schwertmann (1962) suggest

that the high charge smectite is derived through transformation of micaceous minerals, whereas low charge varieties are authigenic, having been derived from weathering of augite, hornblende, feldspars, volcanic detritus or hydrothermal solutions. Churchman (1980) described the authigenic formation of beidellite from dioctahedral mica in a series of Podzolic soils in New Zealand. Scanning electron micrographs indicate the presence of undetermined authigenic minerals, with a smectite-like morphology on the surfaces of both K and Ca-feldspars (Plate 2). The presence of these authigenic minerals was previously postulated by Abder-Ruhman (1980), although he did not have the facilities for chemical analysis to support his hypothesis. Smectites derived from K-containing mica expand to 14 A° with glycerol saturation whereas low charge species expand to 17 - 18 A° (Quakernaat, 1968, cited in Thorez, 1976).

The smectite components of these areas are dominated by dioctahedral species, illustrated by the strong (060) reflection at 1.49 A° - 1.51 A° of samples previously heated to 550° C to thermally decompose the kaolinite and thus remove its interfering 1.50 A° reflection. The presence of a minor amount of a trioctahedral mineral is indicated by a peak between 1.53 A° - 1.54 A°. This may be a biotite or, perhaps, a trioctahedral smectite. Somasiri and Huang (1974) demonstrated that trioctahedral micas are weathered out from the fine clay fraction of Saskatchewan soils. Micas in the less than 0.2 micron fraction were shown to weather to a 2:1 phyllosilicate by Somasiri *et al.* (1971). Jackson and Sridar (1981) described the formation of saponite, a trioctahedral smectite, from biotite. The shoulder at 18.9 - 19.2 A° on the diffractogram of the Ca-saturated glycerol treated specimens suggests the presence of minor amounts of the trioctahedral smectite, saponite, in fine clay separates from both soil units.

Allaway (1949) and Carthew (1955) described the application of differential thermal analysis to differentiate between smectite clay species following saturation with piperidine. This treatment produces a series of exothermic peaks below 300° C representing the combustion of hydrogen from the cracking of the piperidine molecule, with subsequent exothermic peaks resulting from combustion if carbon. Carthew (1955) claims the temperature of carbon combustion is related to positions of piperidine absorption, and to the temperature of dehydroxylation which allows entry of oxygen into the lattice for combustion. The piperidine molecule is absorbed in the interlayer position

Plate 2: Scanning electron micrographs of selected feldspar grains and authigenic "smectite-like" minerals observed on the grain surfaces.

A, B: Micrographs of a weathered microcline grain with authigenic minerals in the dissolution striae on the grain surface. The composition of this mineral, in conjunction with its morphology, indicate that it is an iron-rich smectite.

C, D: Micrographs of an orthoclase grain with clay bridges evident in the weathered zones between the crystal lamellae.

E, F: Micrographs of an anorthite grain with square, irregularly oriented, etch pits developed on the surface. Surface encrustations of amorphous aluminosilicate material are present at the edges of the pits.

G, H: Micrographs of a weathered anorthite grain with authigenic Fe-rich smectite formed in the interior of the irregular etch pits.

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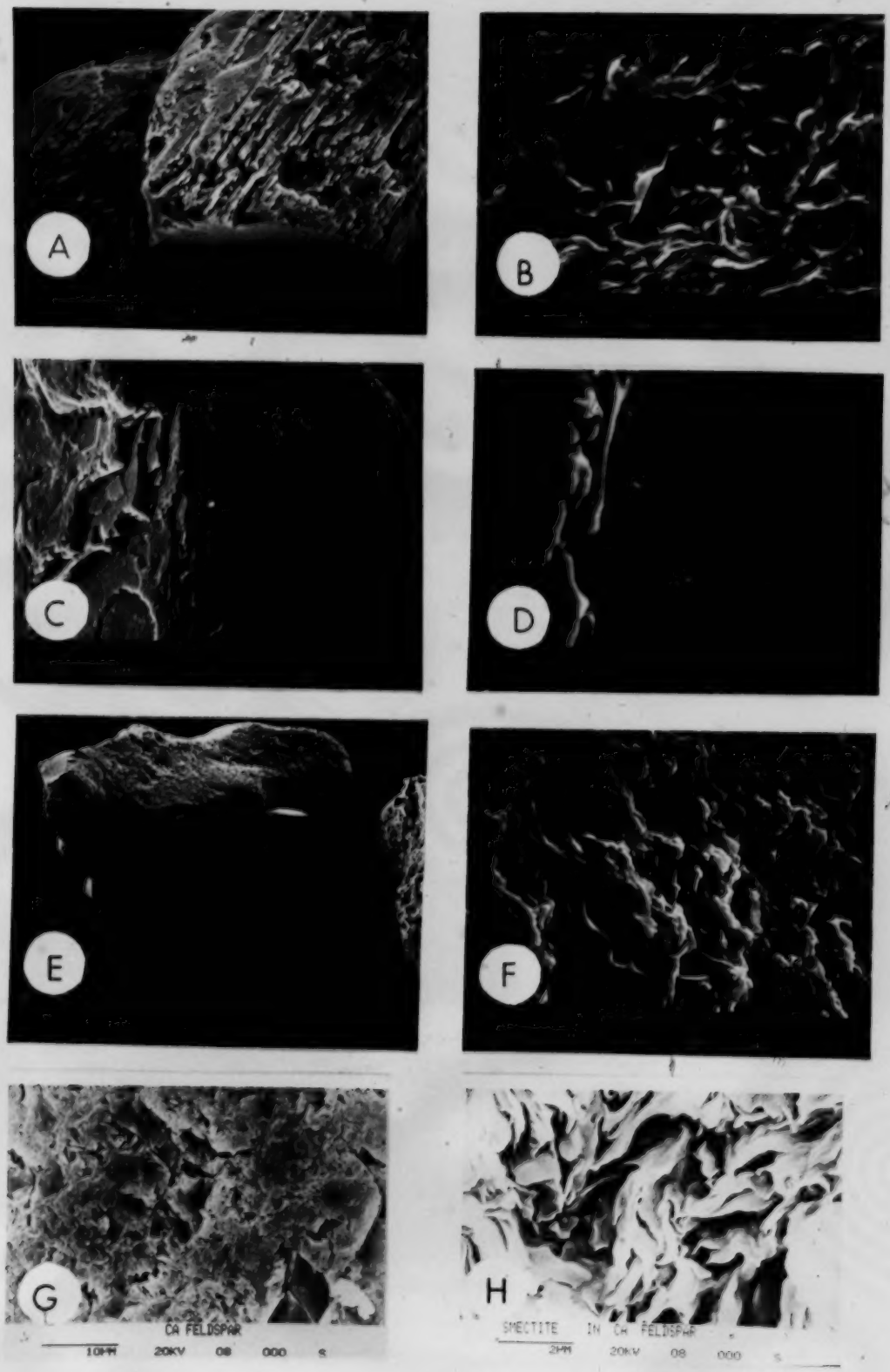
A
B
C
D
E
F
G
CA FELDSPAR
10μm 20KV 08 000
H
SMECTITE IN CA FELDSPAR
2μm 20KV 08 000

of the smectites and is combusted on release of the OH^- when dehydroxylation occurs on heating. Thus the final exothermic dehydroxylation peak of smectites corresponds to the piperidine combustion peak. This combustion peak is sharp in a mixture, whereas the endotherms are often difficult to differentiate (Carthew, 1955). An exothermic peak at 700° C indicates presence of a magnesian smectite, 600° C a smectite with Al in tetrahedral coordination and 450° – 500° C the iron–rich smectite, nontronite (Carthew, 1955).

Differential thermal analysis patterns of both Ca and piperidine saturated fine clay separates from both Legend and Kinosis units are shown in Figures 39 and 40. The patterns of the Ca saturated fine clays show relatively little differentiation in the region of expected endotherms for smectite clays (600° – 800° C). Peaks for pure smectite components in this region were further defined by Schultz (1969). Non–ideal beidellites and non–ideal montmorillonites were found to have endotherms at 560° ± 30° C by Schultz (1969), who related this to an excess of hydroxyl groups (>4) in the lattice structure and suggested that this was only indirectly related to Al substitution in the tetrahedral layer. This non–ideal montmorillonite is the "soil montmorillonite" of Van der Marel (1961). Examination of piperidine saturated clays by Oades and Townsend (1962) found that peaks at 532° C and 655° C were obtained with what they describe as an abnormal montmorillonite. Peaks at 700° C were obtained for dioctahedral montmorillonite and 600° C for beidellite. They also found that illite in clay samples consistently gave exothermic peaks at between 300° – 400° C, and explained this by suggesting that these peaks were related to the combustion of carbon in the external exchange positions.

The DTA pattern of the piperidine saturated Legend sample shows a strong exothermic peak at 600° C which indicates a substantial imbalance of hydroxyl in the smectite clays of this sample and a substantial amount of tetrahedrally substituted Al. This implies that the suggestion of presence of beidellite based on the Greene– Kelley test is correct, although, based on the criteria of Schultz (1969), this is a non–ideal beidellite such as the soil beidellite of Ross and Mortland (1966). The assymetry of the X–ray diffraction peak on the low angle side (550° C treatment) also suggests the presence of soil montmorillonite in this sample . The intensity of the peak at 660° C

confirms the dominance of magnesium-rich smectite in the samples. The shoulder at 440 - 550° C indicates of minor amounts of nontronite.

The patterns from the Kinosis samples do not show the positive presence of the non-ideal beidellite observed in the Legend samples. The exothermic peak occurs at 660° C, with a broad shoulder on the low temperature side being possibly related to a random distribution of the Al in the tetrahedral layer (Schultz, 1969). This indicates that the high amount of beidellite indicated by X-ray diffraction is "ideal" (Schultz, 1969), and the distinction between this species and ideal montmorillonite is not possible on the basis of thermal behaviour. The exothermic shoulder present at 345° C in both regions is attributed to vermiculite.

Infrared analysis of smectites has provided considerable information on their structural properties, with absorption bands aiding in identification individual species (Borchardt, 1977). Silicate minerals have have strong absorption bands (Si-O) near 600 cm^{-1} and 1000 cm^{-1} complicated by considerable variation due to Al substition for Si (White, 1971). In smectites hydroxy bending vibrations cause absorption which is characteristic of the octahedral sheet composition; with absorption bands near 920 cm^{-1} when only Al is present and near 820 cm^{-1} when Fe is dominant (Farmer, 1974). The vibrations of the individual smectite species, which vary in octahedral composition, have been described by Farmer and Russell (1967), White (1971), Farmer (1974). Interpretation of the spectra from the clay separates of this study was based on data in these reviews, and on the standard patterns depicted by Van der Marel and Buetelspacher (1976).

Infrared spectra of representative fine clays from the Legend and Kinosis units are illustrated in Figure 41 along with patterns obtained from standard nontronite, montmorillonite AP11 and montmorillonite H26. The octahedral compositions based on microprobe analyses of these clays are nontronite ($Fe_{3.8}$ $Mg_{0.2}$ $Al_{0.2}$), AP11 ($Mg_{1.03}$ $Fe_{0.1}$ $Al_{2.9}$), H26 ($Mg_{0.32}$ $Fe_{0.41}$ $Al_{3.2}$). The tetrahedral compositions of these clays is essentially identical ($Si_{7.8-7.9}$ $Al_{0.1-0.2}$) (D.G.W. Smith, pers comm) [2]. The waveband data in Table 17 is based on examination of several samples from each region, with data from reference minerals being listed for comparative purposes (Farmer and Russell, 1974).

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[2]Dr.D.G.W. Smith, Department of Geology, University of Alberta

Table 17: Frequency of the infrared absorption bands of the fine clay separates from the Legend and Kinosis Soil Units. The band assignments listed for standard smectite minerals are based on data documented by Farmer et al. (1967, 1974, 1979).

Bond Assignment	Frequency (cm -1) of Absorption Bands				
	Beidellite	Nontronite	Wyoming Bentonite	Kinosis (f.c.)	Legend (f.c.)
Si-O			1118		
	1084	1091	1080	1080	1090
stretch	1041	1034	1048	1040	1030*
	1022	1017	1025	1020	1010m
				935-940	
	942		920	910-915*	910-930m
	872		890	870	860
			870-890		
R-OH		848	849		830-840m
	819	818	800	820-840	800-820
bend	776	786		815	830
					780
	729	753		750	740
				720	720
	693	680		680-695*	690
				650	650
Si-O-R+++	566	587	523	520	520
	537				
and	511	493		500	500*
					490
R+++-OH	479	450	468	440	440*
	426	430		430m	
				425-410	
				385	
				345	345**
OH	3660	3564	3639	3695	3685
				3605	3620
				3540	3560
				3450	

*strong band
m medium band

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The Kinosis spectrum (Figure 41) has strong bands at 690 - 695 cm^{-1} with an associated band at 815 cm^{-1} being interpreted as indicative of nontronite. The band at 420 cm^{-1}, whose intensity is proportional to the iron content (Farmer and Palmieri, 1975), confirms this. The absorption bands at 920 cm^{-1} and 760 cm^{-1} are associated with tetrahedral Al-O vibrations and indicate presence of beidellite. The absorption bands in the 3600 - 3700 cm^{-1} region are due to OH stretching and are characteristic of kaolinite (Farmer, 1974; Kodama 1971), whereas the lower bands at 3500 - 3560 cm^{-1} are related to either Fe^{+++}-OH groups of nontronite or $AlFe^{+++}$-OH groups of an Fe-montmorillonite (Goodman *et al*, 1976). The shoulders present between 830 - 890 cm^{-1} are caused by substitution of Mg and Fe in the octahedral layer. Small peaks at 658 cm^{-1} (Al-O-Si) and 535 cm^{-1} have been related to saponite (Farmer, 1974), as has a weak shoulder at 3710 cm^{-1}. The bands observed at 345 - 350 cm^{-1} have been associated with the presence of poorly crystalline aluminosilicates such as imogolite (Farmer *et al*,1977, 1980; Parfitt *et al*, 1980a, 1980b; Russell *et al*, 1981), but this possibility was not confirmed by any means such as alkaline dissolution or TEM in this study. Recognition of imogolite bands in this region is questionable in the presence of crystalline silicates such as are present in these samples (Dr.V.C. Farmer, pers comm.).[3]

The spectra of the Legend samples (Figure 41) are similar to that of the Kinosis, with a major exception. The bands assigned to the beidellite are much weaker suggesting that it is present in lesser amounts in these samples or that the distribution of the Al in the tetrahedra is irregular. The confirms both the DTA and X-ray diffraction data presented above. The assignments of wavebands to the individual mineral species is tentative in some instances, but when examined in conjunction with the data obtained by X-ray diffraction and DTA the interpretation is supported.

The presence of both beidellite and Fe-rich smectite in the fine clay fraction confirms the findings of Pawluk and Bayrock (1969) in their description of the clay fraction of Alberta tills. This study has, however, been able to relate the smectite species in the fine clay fraction to source lithology. The Legend unit, with its high Cretaceous component, has been shown to have a significant amount of non-ideal beidellite in the fine clay fraction and an associated dominance of montmorillonite. The

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[3]Dr.V.C. Farmer, Macauley Institute for Soil Research, Craigebuckler, Aberdeen.

beidellite of the Kinosis unit, using the criteria defined by Schultz (1969), has been shown to be ideal in its structural form, and to comprise nearly 50 % of the smectite minerals present. The qualitative data summary in Table 18 indicate similar amounts of mica, kaolinite and vermiculite in the fraction of both units. There are also minor amounts of nontronite present in both regions, along with a trioctahedral smectite which displays some of the characteristics which have been associated with saponite. The identification of the different smectite species could be much simplified by use of more particle size separates in conjunction with separation of the paramagnetic members using a flow system such as that described by Schultz and Dixon (1979).

7.1.2 Bulk Clay and Coarse Clay.

X-ray diffraction analyses indicate that the bulk clay separates from the Legend and Kinosis unit can be described as consisting of varying amounts of micaceous minerals, smectites, kaolinite and chlorite. The actual smectite species present in samples from the two regions were differentiated in the previous section. This section will examine in more detail the species composition of the chloritic minerals, the kandites and the micas.

X-Ray diffraction data indicate the presence of chlorite in 67 % Kinosis samples, and 83 % of the Legend samples. The mean of the (001) reflection for Kinosis samples was 14.28 ± 0.34 A°, and that of the Legend samples 14.22 ± 0.33 A°, for the 550° C treatment. Application of the Student's t-test indicated that there was no statistically significant difference between the two values. The (001) and (060) reflections have been cited in the literature as empirical measures of the tetrahedral and octrahedral cation populations of chlorite minerals. Increasing substitution of Al for Si in the tetrahedral sites decreases layer thickness, and is measured by the relationship described by Bailey, (1973).

$$d(001) = c \sin B$$

Increasing substitution of the larger Fe^{++} for Mg^{++} or Al^{+++} tends to increase the lateral dimensions of the layers, as measured by the d(060) spacing. Bailey (1975), in a study of

Table 18. Mineralogical composition of the fine clay fraction of the Legend and Kinosis Soil Units.

	SOIL UNIT	
Mineral	Kinosis	Legend
Smectite	62%	53%
Montmorillonite	++++	++++
Beidellite	+++	++
Nontronite	++	++
Saponite	+	+
Vermiculite	6	2
Kaolinite	10	15
Mica	22	30

++++ Dominant
+++ Major
++ Trace
+ Present (?)

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a range of chlorites, found closest agreement between calculated and measured compositions for the tetrahedral layer using the equations of Brindley (1961):

$$d\,(001) = 14.55\ A^{0} - 0.29\ X \quad (1)$$

Kepezhinkas (1965):

$$d\,(001) = 14.648\ A^{0} - 0.29\ X \quad (2)$$

Bailey (1973):

$$d\,(001) = 14.648\ A^{0} - 0.378\ X \quad (3)$$

where x represents the number of Al atoms substituting for Si in the tetrahedral layer. Prediction of the tetrahedral composition based on these equations is given (Table 19).

Diffractograms, recorded at $1/8^{0}$ 2 θ min^{-1}, obtained from samples heated to 550^{0} C give a (060) reflection of 1.5607 A^{0} for both Kinosis and Legend Units, which indicates that the chlorites are trioctahedral. Van Englehardt (1942) (4) and Kepezhinskas (1965) (5) describe equations relating the b parameters (where b = 6*(060)) to octahedral composition

$$b = 9.22\ A^{0} + 0.028\ Fe^{++} \quad (4)$$

The Fe^{++} is the number of Fe atoms per 6.0 octahedral positions.

$$F = 527.025\ b - 39.461\ d\,(001) - 4283.797 \quad (5)$$

where F is the ferruginosity or heavy atom content in atomic percentages (Table 19).

The number of heavy octahedral atoms, mainly Fe, in the 2:1 mica like layer (Fe ml),minus those in the brucite-like interlayer (Fe bl) hydroxide sheet, was estimated from the intensity ratio of the third and fifth order peaks (I_{003} / I_{005}) using the curve developed

Table 19. Calculated compositions of the octahedral and tetrahedral layers of the chlorite minerals present in the clay separates from the Legend and Kinosis Soil Units.

		SOIL UNIT	
	Equation	Kinosis	Legend
Tetrahedral Composition	(1)	(Si 3.07 Al 0.93)	(Si 2.86 Al 1.14)
	(2)	(Si 2.73 Al 1.27)	(Si 2.54 Al 1.46)
	(3)	(Si 3.03 Al 0.97)	(Si 2.87 Al 1.13)
Octahedral Composition	(4)	(Al 3.14 Fe 2.86)	
Ferruginosity	(5)	54 %	56 %

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by Petruk (1964). The degree of asymmetry (DA), which may be expressed by the following equation,

(Fe ml − Fe bl) = DA,

gives an indication of the relative distribution of Fe in the two types of octahedral position. For symmetrical distribution of Fe in the two octahedral sites, the degree of symmetry is equal to 0. The average degree of asymmetry obtained from several random powder XRD patterns was 0.75, indicating that there was more Fe in the octahedral sites of the 2:1 units than in the interlayers of these chlorites.

Presence of kaolinite was confirmed in both regions by the persistence of the 7 A° peak following dissolution of the trioctahedral chlorite with dilute (2N) HCl . Kodama and Oinuma (1963) describe the use of the 3968 ± 2 cm^{-1} absorption band for infrared spectra of clay separates for identification of kaolinite in mixtures containing chlorite. This band, due to free hydroxyl stretching in the kaolinite lattice, is present in the representative spectra from both units (Figure 42). The presence of the relatively distinct band at 2652 cm^{-1} may be indicative of dickite in the Kinosis samples. Hoeve *et al* (1981) noted the presence of dickite as a component of the interstitial clays in the Athabasca Group sandstones and conglomerates to the north−east of the study area. Dickite, which has a two layered monoclinic cell, has higher order reflections (4.27 A°, 3.95 A°, 3.42 A°, 3.27 A°, 2.79 A°) which have no parallel in kaolinite (Thorez, 1976). These reflections are present in powder diffractograms of the bulk and coarse clays of the Kinosis samples, but could not be identified in the Legend separates .

The crystal structures of kaolinite minerals are frequently disordered with the different layers of the crystals being distorted in the direction of the crystallographic b−axis by an amount $n.b_o/3$. Brindley (1961) showed that increasing structural disorder can be observed in X−ray diffractograms by a diffusion of the six reflections between the (001) and (002) basal spacings, and by a broadening of the reflections of d−spacings less than 2 A°. There have been several methods described for the calculation of an empirical "crystallinity index" for kandites based on X−ray diffraction data (Hinckley, 1963; Hughes and Brown, 1979; Hughes, 1980), but application of these was found to be impractical for samples of this study either because of poor peak resolution of the powder diffractograms, or because of interference of the quartz reflection at 4.27 A° in

the calculation of the "Hinckley Index." Comparison with powder data in Brown (1961) does, however, indicate that the kaolinite in the parent materials in this region of north-east Alberta is b-axis disordered. Smykatz-Kloss (1975) described a relationship between the dehydroxylation temperature of kaolinite and an index of crystal order. The mean dehydroxylation temperature of 548 ± 8° C for both units is equivalent to a value of 41 % based on the index of Smykatz-Kloss (1974). This value means the kaolinites in these clay separates are strongly disordered, and this disorder has been related to isomorphous substitution and vacant sites in the octahedral layer (Brown, 1961).

Different polytypes of a given group of layer silicates (eg micas) have essentially the same lateral unit cell dimensions (a and b), differing only because of indexing on different types of unit cells (Bailey, 1975). The polytypes often differ in their c dimension where the true repeat distance is an integral of the unit structure thickness. The mica poplytypes are determined primarily by differences in the octahedral sheet of different layers, since the tetrahedral sheets of adjacent layers essentially superimpose in the interlayer in order to fit around the interlayer cation. Bailey (1967) has shown that there are two different sets of octahedral cation sites that may be occupied and three different directions that one tetrahedral sheet may be shifted relative to the other for each set. Only certain of these theoretical polytypes are common in nature (Smith and Yoder, 1956; Bailey, 1966, 1967). These are the 1M and 2M1 polytypes which are both monoclinic with the 1M having a repeat every layer, and 2M1 a repeat every other layer. These, and the 3T polytype, have interlayer stacking angles of 120°. The 2M1 polytype, formed at higher temperatures, appears to be the dominant dioctahedral form. Low temperature authigenic dioctahedral micas are of the 1M or 1Md polytype. Tables showing the characteristic X-ray reflections of these polytypes are listed by Thorez (1976) and Fanning and Keramidas (1977).

Random powder X-ray diffractograms of clay separates which had been ignited at 550° C indicated that the suite is dominated by dioctahedral minerals (mica has a (060) spacing at 1.50 A°), although a relatively strong reflection at 1.536 A° indicates trioctahedral mica also. Examination of the X-ray powder diffractograms indicated that both 2M1 and 1M polytypes were present in the Kinosis and Legend soil units. Intensities of the common reflections of the polytypes (after Kodama (1962) as cited in Thorez

(1976)) indicated that the ratio of 2M1 : 1M was approximately 2 : 1 for both units, although the 1M was slightly more abundant in the Legend unit. It was impossible to differentiate the presence of the 1Md polytype in either unit.

Examination of the 10 A° peak of all the samples from the two units indicates a slight degree of asymmetry on the low angle side, and an accompanying asymmetry on the high angle side of the peak at 3.5 A°. This implies that there is some depotassification in the micaceous minerals in all samples. Calculation of the "sharpness ratio" (Weaver, 1960) demonstrated that the degree of depotassification was approximately the same for both soil units (Legend = 2.4 ± 0.3; Kinosis = 2.5 ± 0.3). The mean values of I_{001} / I_{002} give an average octahedral composition of approximately ($Al_{1.75}$ $Fe_{0.25}$) for the hydrous mica using the curves of Grim (1968), (Kinosis I_{001} / I_{002}) = 1.06 ± 0.13; Legend I_{001} / I_{002} = 1.11 ± 0.28). These ratios are less than the 1.6 calculated from the diffractograms calculated from the diffractograms presented by Abder-Ruhman (1980) for parent materials some 200 miles south of the study region. This difference may be attributed to a higher degree of depotassification of the micaceous minerals in the southern tills. This ratio approximates a K_2O content of 10.6 % for the micaceous minerals of the parent materials of the present study region based on the graphs presented by White (1962), which is a value similar to that suggested by Jackson (1973) for the estimation of micaceous mineral content in soil clay separates.

Infrared spectra of bulk and coarse clay separates (Figure 42) show some differences from those of the fine clay separates. The major difference being the strong absorbances which are indicative of the presence of kandite species. There is also a strong doublet at 785 and 800 cm^{-1} which is characteristic of the presence of quartz in the samples. The balance of the bands defined in the spectra can be assigned to the specific atoms in the clay structures but the mineralogy is too complex to attempt definite clay species characterisation. The vibrations in the 1000 - 1120 cm^{-1} are caused by SiO stretching of the tetrahedra of all the clay species present, and the 900 - 950 cm^{-1} vibrations are OH bending. The strong 915 cm^{-1} is probably linked to $2Al^{+++}$, as are the 935 and 945 cm^{-1} bands in all spectra. The 860 cm^{-1} band in the Kinosis sample spectrum is linked to Al^{+++} Mg^{++} OH bending, with the other shoulders in this region ascribed to the same bonds. The 810 - 830 cm^{-1} bands are indicative of Fe^{+++}-OH

vibrations and the adjacent 840 cm^{-1} band is from Al^{+++} Mg^{++}–OH bending. The bands in the 690 cm^{-1} region are caused by Si–O vibrations, and are probably related to the minor quartz in the samples (Farmer and Palmieri, 1975). The 630 cm^{-1} band in the coarse clay from the Kinosis sample is from Al^{+++}–O stretching, and the 520 cm^{-1} bands are indicative of Fe^{+++}–O stretching with the strong 500 cm^{-1} band reflecting Si–O deformation. The 450 cm^{-1} is linked to Fe^{++}–O–Si stretching, with the shoulder at 410 – 420 cm^{-1} due to Si–O–Mg^{++} deformation. The medium intensity bands at 390 and 360 cm^{-1} are caused by Al^{+++} lattice vibrations. These assignments to individual lattice compositional variations are based primarily on the review article of Farmer and Palmieri (1975), with additional data being obtained from published spectra. As was mentioned in the previous section, assignment to specific minerals would only be tentative, and is thus not generally attempted here.

The aplication of differential thermal analysis to identification of various smectite species was described in the previous section and the DTA patterns (Figures 39, 40) do not extend the information described previously. The pattern of the Legend coarse clay fraction shows exotherms at 660° C and 692° C. The absence of the lower temperature peak at about 600° C observed in the fine clay samples suggests that the non–ideal beidellite is in the fine clay only and the montmorillonite is the dominant smectite of the coarse fraction. The coarse and bulk clay patterns of the Kinosis unit samples are essentially the same as the patterns of the fine clay from the same unit, confirming the presence of ideal smectites (Schultz, 1969). All bulk patterns in Figures 39 and 40 have prominent shoulders in the 345 – 380° C region which, based on the data of Oades and Townsend (1962), indicates the presence of hydrous mica. The shouder ascribed to nontronite in the fine clays is not present in these patterns thus confirming the fact that this smectite species is a relatively minor component of the clay mineral suite of these regions.

This discussion of the coarse and bulk clay separates has demonstrated the similarity of the detrital micaceous minerals in the two soil unit parent materials under discussion. It has described the probable chemical compositions of the tetrahedral and octahedral layers of these minerals by application of documented analyses and graphs relating chemical composition to X–ray diffraction characteristics of the individual

species. The same technique has been documented and applied here to the chlorite minerals detected in the clay fraction of the samples from the study region. The presence of dickite was confirmed for the Kinosis unit samples only, and the kaolinites were found to be b-axis disordered, which implies that they have not been heated to a temperature in excess of 200° C (Smykatz-Kloss, 1974) during diagenesis of the sediments from which they are inherited.

7.1.3 Conclusion:

Routine clay characterisation analyses for the soil parent materials within the study region indicated quantitive differences in the amounts of the dominant mineral groups in the different mapped units. The major discriminating minerals were the micas and the kaolinite+chlorite grouping, with the Legend unit separated from the other three by Duncans Multiple Range Test. Isotopic analyses of clay separates from selected samples indicated significant differences in the signature of the suites from the Legend unit as compared with the other three. Detailed mineralogical analyses of representative samples from the Legend and Kinosis units demonstrated subtle mineralogical differences which can be related to source lithologies of the glacial sediments.

The detrital micas are essentially similar in both regions indicating that the Cretaceous formations incorporated into the Legend unit must have, in turn, inherited much of their material from the Shield. There are quite marked differences in the smectite component between the two units. The Kinosis unit smectites consist of approximately equal amounts of ideal beidellite and ideal montmorillonite, whereas the Legend unit smectites have a lesser amount of beidellite, which is non-ideal in composition, and a correspondingly higher amount of ideal montmorillonite. The DTA characteristics of the montmorillonite in the Legend unit sediments indicate more Mg in the octahedral layer than that of the Kinosis unit, a difference which which may be related to the formation of the mineral in the Legend unit in the presence of seawater. This formation in a marine environment is probably the cause of the difference in isotopic signature of the clay fraction of these two units.

Both units contain minor amounts of nontronite in the fine clay fractions. The micaceous minerals are primarily dioctahedral, with a lesser amount of trioctahedral mica.

The latter, however,is not present in the fine clay fraction and is thought to be the source of the minor amount of triocthedral smectite identified in the fine clay fraction from both regions. This trioctahedral smectite has the characteristics of saponite. The micas were found to be of the 2M1 and 1M polytypes and to have undergone a minor amount of depotassification. Composition of the chloritic component was estimated on the basis of lattice parameters calculated from X-ray diffraction characteristics. This technique was also applied to estimate the composition of the octahedral and tetrahedral layers of the micas.

7.2 CLAY SEPARATE CHEMICAL ANALYSIS:

In addition to the various mineralogical analyses presented in the previous section for the 46 individual samples, chemical composition data were obtained for 20 elements using the methodology outlined in the Appendices VII and VIII. Data for Si was initially obtained by difference, and checks on some 25 samples by suspension aspiration indicated that the mathematically derived data was generally within 3–4 % of the analytical results,i.e. the analytical value for a sample was 31 %, whereas the mathematical value was 29.8 %. The discussion in the appendix indicates that the analytical data from suspension analysis are on a water–free basis, thus implying that the mathematical data presented in Table 20 for Si are accurate within experimental limits for the 550° C sample base weight used for all calculations.

7.2.1 Relationship of Clay Chemistry to the Soil Units.

The discussion of Soil Unit differentiation indicated that ANOVA techniques were utilised to partition the variance within and between the surficial units. The ANOVA program available in the SPSS package of statistical programs (Nie *et al*, 1975) was utilised to perform a one–way analysis of variance to determine whether the analysed chemical variables differ significantly between the four units. The variables (elemental compositions) were found to differ between the units at the 0.05 level were Cu, Cr, Zn, V, P, K, Fe, Al, Ni, Si. (Appendix V)

Mean values for the clay compositional chemistry are listed for the major Soil Units in Table 20. Although several of these elemental levels (Cr, Ni, P and Zn) differentiate between the Legend and Kinosis Units , there is no element suitable for the regional differentiation of the clay separates based on the application of Duncan's New Multiple Range Test (Steele and Torrie, 1980) (Table 20). The Legend and Kinosis Units have already been shown to have a diverse sediment provenance.

The lack of clear distinction between the different units using individual variables, and the internal complexity of the intervariable relationships (Table 21) suggests that the use of numerical taxonomy methods may prove useful. Data analysis was approached from two different viewpoints:

1. Discriminant analysis was used to distinguish between the *a priori* established

Table 20: Modal chemical composition of the clay separates of the major Soil Units in the study region.

	DOVER	KINOSIS	HORSE RIVER	LEGEND	REGION
	Major elements (%)				
Al	9.45 a	11.67 bc	11.18 b	12.37 c	11.18
Ca	1.47 a	1.27 a	2.31 a	1.76 a	1.71
Fe	4.40 a	6.41 b	5.97 b	6.41 b	5.87
K	1.99 a	2.08 a	2.53 b	3.05 c	2.41
Mg	1.03 a	1.13 ab	1.21 b	1.09 ab	1.12
Na	0.33 b	0.22 a	0.25 a	0.22 a	0.25
Ti	0.30 a	0.35 b	0.32 a	0.31 a	0.32
	Minor Elements (ug / gm)				
B	199 a	232 ab	255 b	239 b	232
Co	17 a	18 a	21 ab	24 b	20
Cr	90 a	114 b	114 b	142 c	115
Cu	53 a	90 b	83 b	88 b	79
Mn	236 a	315 b	302 b	198 a	265
Mo	2.6 a	4.6 b	3.7 b	4.8 b	3.9
Ni	66 a	88 b	81 b	104 c	85
Pb	40 a	47 b	45 ab	42 ab	44
Sr	283 ab	311 ab	268 a	352 b	303
V	171 a	233 b	238 b	385 c	256
Zn	93 a	139 b	141 b	165 c	135
C.E.C.	43 a	44 ab	52 b	46 ab	46
K.E.C.	35 a	36 a	37 a	44 b	38
S.A.	371 a	475 b	433 b	543 c	455

Elements followed by the same letter are not significantly different at the 0.05 level based on Duncan's New Multiple Range Test.

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Table 21. Correlation matrix of elemental compositional levels of the clay separates of the major Soil Units of the study region.

	CU	CO	B	CR	PB	ZN	MN	V	SR	MO	P	NA	K	MG	FE	AL	TI	NI
CO	0.40																	
B	0.38																	
CR	0.53	0.54	0.41															
PB	0.27																	
ZN	0.67	0.49	0.34	0.78														
MN					0.35													
V	0.52	0.59	0.31	0.93		0.69	-0.34											
SR	0.33																	
MO	0.42		0.31	0.67	0.37	0.64		0.53										
P	0.50	0.51		0.78		0.69		0.83	0.31	0.54								
NA	-0.32			-0.65		-0.59		-0.49		-0.58	-0.43							
K	0.43	0.58	0.35	0.59		0.49	-0.31	0.69			0.65							
MG	0.42				0.35	0.49	0.43											
FE	0.54	0.31	0.41	0.84	0.32	0.77		0.65		0.81	0.59	-0.77		0.34				
AL	0.48	0.39	0.45	0.89		0.73		0.73		0.74	0.64	-0.78	0.45		0.90			
TI					0.47		0.58			0.41		-0.38		0.35	0.51	0.40		
NI	0.61		0.32	0.70		0.82		0.63		0.57	0.59	-0.63	0.37		0.71			
SI	-0.54	-0.48	-0.42	-0.82		-0.75		-0.70		-0.75	-0.70	0.70	-0.43	-0.34	-0.84	-0.87		-0.67

Only correlation coefficients above 0.30 listed.

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groups on the basis of the measured variables, and provided criteria for delineating the best variables for differentiating group means.

2. Factor analysis was utilised to describe the major features of chemical variation, on the assumption of a random data set.
3. Cluster analysis was used to group the clay separates according to chemical composition, which was, in turn, related to source or sedimentological unit.

7.2.2 Application of Discriminant Analysis.

Discussion on the application of this method to the Earth Sciences has been given in May (1972). The subprogram DISCRIMINANT, available in the SPSS package of statistical procedures (Nie *et al*, 1975), was utilised for data analysis. The data was analysed in two ways. The first was based on the Legend and Kinosis units to define the linear function to best describe the group membership in terms of the chemical variables, and to determine the affinity of the Horse River and Dover units to the other two in terms of dominant source of sediments. The second was to use a multigroup approach , which is more difficult to understand at the intuitive level (Nie *et al* , 1975), although the mathematical manipulations are the same. This produced three discriminant functions describing group membership, and a summary table describing the statistical accuracy of the *a priori* classification. The selection criterion used in the calculations was based on the maximization of the smallest F ratio between the group pairs in order to maximize the Mahalonobis distance between the two closest groups. The following discussion relates primarily to the standardized discriminant functions, as the standardized coefficients indicate the importance of the individual variables in the function.The unstandardized classification functions for the individual groups are described in the accompanying tables.

A discriminant analysis based on the Legend and Kinosis units only (Table 22) indicated that the *a priori* classification was correct with the following discriminant function being calculated:

$$D = -1.3B - 0.1Zn + 1.7Mn + 5.8V - 0.3Sr - 1.1Mo$$
$$+ 0.6Na + 1.2Ca + 1.2Mg - 1.9Fe + 1.1Ti + 3.3Ni$$

Table 22. Results of a discriminant analysis of the clay separate chemical compositional data for the Legend and Kinosis Soil Units.

CLASSIFICATION FUNCTION COEFFICIENTS

	KINOSIS	LEGEND
B	-1.18	-1.48
ZN	-2.25	-2.78
MN	1.25	1.50
V	4.92	5.95
SR	-0.62	-0.81
MO	-50.08	-57.68
NA	743.24	896.89
CA	35.74	42.33
MG	857.78	985.49
FE	-90.18	-113.23
TI	2841.40	3282.65
NI	11.15	13.67
(CONSTANT)	-1559.23	-2116.38

CANONICAL DISCRIMINANT FUNCTIONS

PERCENT OF VARIANCE	CUMULATIVE PERCENT	CANONICAL CORRELATION	CHI-SQUARED
100.0	100.0	0.98	55.285

CANONICAL DISCRIMINANT FUNCTION COEFFICIENTS

	STANDARDISED	UNSTANDARDIZED
B	-1.28	-0.03
ZN	-1.09	-0.05
MN	1.68	0.02
V	5.68	0.10
SR	-1.28	-0.02
MO	-1.08	-0.72
NA	0.62	14.45
CA	1.22	0.62
MG	1.12	12.04
FE	-1.86	-2.17
TI	1.14	41.61
NI	3.29	0.24
		(CONSTANT) -52.54

GROUP CENTROIDS

GROUP	FUNCTION
1	-5.30
2	5.30

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The canonical correlation of this function is 0.98, and the Total Discriminating Power (TDP) is 0.966 (Tatsnoka, 1970). The TDP has been compared with the R^2 in a linear regression and thus indicates the significance of this discriminant function. Examination of this function indicates that the elements with the most discriminating power are V, Ni, Fe, Mn, Sr, B. Potter *et al* (1962) showed that B, Cr, Cu, Ga, Ni and V were more abundant in marine than in fresh water argillaceous sediments. If the parallel is drawn with this study, the implication is that the continental authigenic clays are depleted in the discriminating elements when compared to those of marine origin in the Cretaceous source material of the Legend unit. These elements are probably enriched in the smectite minerals (or X-ray amorphous compounds), as it has been shown in the previous section of this thesis that the micaceous and kaolinitic minerals in the two parent material units are similar. The presence of Fe and Mg in the function with the minor elements suggests that there is substitution in the octahedral layer of the smectite minerals to cause this differentiation.

A second analysis based on the four groups in this study (Table 23) indicates that 86.96% of the samples were correctly classified based on the total chemical composition. Examination of the discriminant scores for the misclassifed samples and the associated territorial classification map indicates that these six samples all fall along group boundaries, with their second highest group probability being that assigned on the basis of field mapping. The five misclassified samples are: 46 (reclassified as Horse River), 15 (reclassified as Horse River), 23 (reclassified as Legend), 28 (reclassified as Kinosis) and 39 (reclassifed as Kinosis).

The two Legend clay samples reclassified as belonging to the Kinosis unit (28, 39) on the basis of their chemical composition are on the north east flanks of Birch Mountains. Their location indicates that they may not have the quantity of Cretaceous sediments incorporated into their till matrix as those samples further to the southwest. These two samples are in an erosive rather than depositional sites. The discriminant analysis does indicate that their second highest probability of group membership is the Legend unit. Sample 46 (reclassified as Horse River) was taken from mixed lacustrine sediments and the classification as Dover represents a mapping oriented decision, such as could arise with any of the samples taken along the boundaries of the Glacial Lake

Table 23. Results of a multigroup discriminant analysis of the clay separate chemical compositional data for the four major Soil Units of the study area.

CANONICAL DISCRIMINANT FUNCTIONS

PERCENT OF VARIANCE	CUMULATIVE PERCENT	CANONICAL CORRELATION	CHI-SQUARED
52.29	52.29	0.89	71.043
33.97	86.26	0.84	25.371
13.74	100.00	0.70	

STANDARDIZED CANONICAL DISCRIMINANT FUNCTION COEFFICIENTS

	FUNC 1	FUNC 2	FUNC 3
CU	0.08	-1.04	0.57
B	0.30	-0.20	-0.52
PB	-0.30	-0.29	-0.15
V	-1.34	0.55	0.11
NA	0.25	1.10	0.28
K	0.11	-0.04	-0.75
MG	0.21	-0.04	-0.63
FE	1.21	-0.34	-0.80
AL	0.06	0.17	1.48
TI	-0.27	0.10	0.52
NI	-0.59	0.78	0.27
SI	0.40	0.09	0.65

UNSTANDARDIZED CANONICAL DISCRIMINANT FUNCTION COEFFICIENTS

	FUNC 1	FUNC 2	FUNC 3
CU	0.04	-0.06	0.03
B	0.71	-0.004	-0.01
PB	-0.05	-0.05	-0.02
V	-0.02	0.01	0.002
NA	5.1	22.7	5.8
K	0.21	-0.08	1.46
MG	1.55	-0.26	-4.58
FE	1.25	-0.34	-0.83
AL	0.05	0.15	1.33
TI	-9.09	3.54	17.58
NI	-0.04	0.05	0.02
SI	0.23	0.05	0.38
(CONSTANT)	-5.01	-6.51	-20.38

GROUP CENTROIDS

GROUP	FUNC 1	FUNC 2	FUNC 3
1	1.84	2.17	0.26
2	0.47	-1.64	1.18
3	0.92	-1.09	-1.47
4	-3.00	0.66	-0.08

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MacConnell basin. Both samples 14 and 44 fall in the boundary areas of the Horse River and Legend units. Sample 23, on the other hand, is taken from the middle of the Horse River unit and the reclassification cannot be simply explained, although the second group membership predicted is again the Horse River unit. The discriminant functions are shown in Table 23.The discriminating variables separated from the original 20 are Cu, B, Pb, V, Na, K, Mg, Fe, Al, Ti, Ni and Al. The major elements in this list are obviously reflecting facets of the mineralogical variation described in the previous section, and the minor elements may be reflecting isomorphic substitution for the major cations in the clay mineral lattices, a suggestion which will be examined in a later section. The elements V, Fe, B and Ni are again important in this equation, with K and Al also having large coefficients indicating that the micaceous minerals are also important in this more complex classification calculation.

Both Duncan's New Multiple Range test and the univariate F ratios of the discriminant analysis indicated that the significant variables describing most of the regional variation in clay mineral composition were Cu, Cr, Mn, Ni, P, V and Zn in the minor elements and Al, Fe, K, Na and Si in the major elements. Thus these variables were used to determine a discriminant function to first test the feasibility of using trace elements only to differentiate the Legend and Kinosis units.(Table 24) The analysis yielded the following function:

$$Di = 1.83\,V - 1.09\,Cr + 0.83\,Ni$$

The canonical correlation of this function is 0.87 and the TDP is 0.73. Application of this function again showed that sample 28 has greater affinity to the Shield provenance in spite of the geographic location. The classification function (Table 24) could be applied to any of the samples from, say, the Dover unit to determine the source lithology of that sample. The selection of V, Cr and Ni from the trace elements as the most effective discriminating variables again confirms the enrichment of V and Ni in the Cretaceous sediments whereas the Cr is enriched in the samples from the continental shield source.

The major elements described above as being significantly different between the sample units were also examined to determine their suitability as variables for

Table 24. Results of a discriminant analysis using the minor element compositional data from the Kinosis and Legend Soil Units.

CLASSIFICATION FUNCTION COEFFICIENTS
(FISHER'S LINEAR DISCRIMINANT FUNCTIONS)

	SUBFILE KIN	SUBFILE LEG
CR	0.98	0.72
V	-0.12	-0.01
NI	0.25	0.45
(CONSTANT)	-54.07	-71.91

CANONICAL DISCRIMINANT FUNCTIONS

	CANONICAL CORRELATION	CHI-SQUARED
	0.86	28.42

STANDARDIZED CANONICAL DISCRIMINANT FUNCTION COEFFICIENTS

CR	-1.09
V	1.83
NI	0.83

UNSTANDARDIZED CANONICAL DISCRIMINANT FUNCTION COEFFICIENTS

CR	-0.08
V	0.03
NI	0.06
(CONSTANT)	-5.38

GROUP	CENTROID
1	-1.66
2	1.66

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discrimination between the Legend and Kinosis parent material unit clay fractions (Table 25). The resultant discriminant function given below has a canonical correlation of 0.75 and a TDP of 0.53.

$$Di = 0.90\ K - 0.61\ Si$$

This demonstrates that the clay major element chemistry is not as effective for provenance separation. The K value is directly related to mica content and the Al probably to smectite content. Neither of these minerals was shown to be overly effective at unit separation using Duncan's New Multiple Range test in the discussion of clay mineralogy. The classification based on this analysis successfully classified all the samples from the Kinosis unit, but misclassified four from the Legend unit. This is the only analysis to produce misclassification of the latter unit.

The same seven minor elements listed for the above calculations were used for a four group discriminant analysis (Table 26). The results for this analysis demonstrate the similarity of the Kinosis, Horse River and Dover units as 16 of the 34 samples in these groups were misclassified on the basis of the minor elements, whereas only one sample was reclassified in the Legend unit (28). The elements selected (Cr, Mn, V, Ni) again reflect the enrichment of Cr in the Shield provenance clay separates, with Mn, V and Ni being enriched in the Cretaceous dominated Legend unit. The overlap between the three units is described by Webster (1977) as being common in trying to discriminate between map units if too few variables are used for the mathematical manipulations. Discriminant analysis based on the major elements (Table 27) produced a classification confirmation for 31 of the 46 samples , with the Legend unit having the highest number of misclassified samples (50 %), confirming the observation made above that the major elements are not strong provenance discriminating variables, although they do discriminate relatively well between the units with a high Shield clay fraction component. The TDP of this analysis is only 0.67, and Na, K, Al and Si were the chosen variables, again indicating that separation is related to the micaceous component.

Application of discriminant analyses to these preclassified units confirmed the strong separation between the Kinosis and Legend units, with the similarities beuween the

Table 25. Results of a discriminant analysis using the major element compositional data from the Kinosis and Legend Soil Units.

CLASSIFICATION FUNCTION COEFFICIENTS
(FISHER'S LINEAR DISCRIMINANT FUNCTIONS)

	SUBFILE KINOSIS	SUBFILE LEGEND
K	1.29	4.92
SI	12.10	11.24
(CONSTANT)	-175.86	-161.14

CANONICAL DISCRIMINANT FUNCTIONS

	CANONICAL CORRELATION	CHI-SQUARED
	0.75	17.24

CANONICAL DISCRIMINANT FUNCTION COEFFICIENTS

	STANDARDISED	UNSTANDARDISED
K	0.90	1.68
SI	-0.61	-0.40
	(CONSTANT)	6.81

GROUP	CENTROID
1	-1.08
2	1.08

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Table 26. Results of a multigroup discriminant analysis using the minor element compositional data from the four major Soil Units of the study region.

CANONICAL DISCRIMINANT FUNCTIONS

PERCENT OF VARIANCE	CUMULATIVE PERCENT	CANONICAL CORRELATION	CHI-SQUARED
82.64	82.64	0.85	18.588
16.19	98.83	0.58	1.5096
1.17	100.00	0.19	

STANDARDIZED CANONICAL DISCRIMINANT FUNCTION COEFFICIENTS

	FUNC 1	FUNC 2	FUNC 3
CR	-0.34	1.16	-0.69
MN	-0.12	0.74	-0.08
V	1.08	-0.69	-0.07
NI	0.45	-0.18	1.06

UNSTANDARDIZED CANONICAL DISCRIMINANT FUNCTION COEFFICIENTS

	FUNC 1	FUNC 2	FUNC 3
CR	-0.002	0.08	-0.05
MN	-0.02	0.01	-0.001
V	0.02	-0.01	-0.001
NI	0.03	-0.01	0.07
(CONSTANT)	-4.65	-7.86	0.18

GROUP CENTROIDS

GROUP	FUNC 1	FUNC 2	FUNC 3
1	-1.68	-0.96	0.02
2	-0.44	0.72	0.24
3	-0.55	0.58	-0.28
4	2.48	-0.36	-0.0004

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Table 27. Results of a multigroup discriminant analysis using the major element compositional data from the four major Soil Units of the study region.

CANONICAL DISCRIMINANT FUNCTIONS

PERCENT OF VARIANCE	CUMULATIVE PERCENT	CANONICAL CORRELATION	CHI-SQUARED
78.95	78.95	0.80	59.23
16.48	95.43	0.52	17.09
4.57	100.00	0.31	4.05

STANDARDIZED CANONICAL DISCRIMINANT FUNCTION COEFFICIENTS

	FUNC 1	FUNC 2	FUNC 3
NA	0.57	-0.38	0.65
K	-0.57	-0.74	0.14
AL	0.29	0.79	0.14
SI	0.66	0.57	1.02

UNSTANDARDIZED CANONICAL DISCRIMINANT FUNCTION COEFFICIENTS

	FUNC 1	FUNC 2	FUNC 3
NA	11.89	-7.92	13.55
K	-1.12	-1.44	0.26
AL	0.26	0.71	1.47
SI	0.39	0.31	0.60
(CONSTANT)	-14.60	-11.54	-38.06

GROUP CENTROIDS

GROUP	FUNC 1	FUNC 2	FUNC 3
1	2.07	-0.35	0.14
2	-0.02	0.98	0.14
3	-0.46	-0.32	-0.51
4	-1.47	-0.37	0.33

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Kinosis, Dover and Horse River units being shown to be strongly related to both minor and major element composition. The elements which were shown to be the best discriminating variables were explained in light of source enrichment during the authigenic formation of the smectite and amorphous clays. The elements, V, Ni, B, Mn, Zn and Fe, which were selected in the discriminant functions have been found to be enriched in marine sediments (Potter *et al*, 1962) and use of these in clay analyses could be useful in any study where diverse sediment provenance is a possibility.

7.2.3 Principal Component Analysis:

This section will briefly examine the application of PCA, a technique commonly used in numerical taxonomical studies, to analysis of intervariable relationships. Prior to analysis all chemical variables were standardised to give a mean of zero and a standard deviation of unity. The PCA mathematics were briefly described in the methodology section, and are reviewed in detail by Harman (1967), Davis (1973) and Kaiser (1970).

Examination of the correlation matrix (Table 21) indicates that Si is negatively correlated with all elements except Na, with any coefficient greater than 0.37 being significant at the 0.01 level. Of the other major elements, both Fe and Al show high correlation coefficients with the trace elements indicated in the ANOVA tables as accounting for significant differences between the clay fractions of the parent materials of the soil units within the study area. The interrelationships between the trace elements are varied and complex, probably being related to both mineralogy and sample site location. Rather than examine each relationship in detail factor analysis was utilised as a data reduction technique.

The calculations involved in factor analysis essentially reduce the correlation matrix to define a set of uncorrelated factors which explain the maximum possible amount of data variation (Harman, 1967; Kaiser, 1970), and then eliminates any of those components which explain only an insignificant portion of the variation. A final step rotates the components (or factors) to associate them with groups of the original variables. The FACTOR program in the SPSS package (Nie *et al*, 1975) was used with the principal component approach and Varimax rotation.

The chemical compositional data from analyses of clay separate were examined by application of three different analytical strategies. The first involved the 20 elemental compositional variables simultaneously, while trace elements were separated from major elements in subsequent analyses and examined independently. The extracted component matrices, eigenvalues and explained variances from this series of analyses are summarised (Tables 28,29,30) in the above sequence. Examination of these tables illustrates the interrelated variables as members of the same component, with the loading by the individual elements on each component being a measure of its importance in the computation of this factor. In the earth sciences these individual components are generally interpreted as geochemical, mineralogical, hydrological or provenance explaining vectors. The discussion describing the PCA results focuses on the Principal Component matrix prior to Varimax rotation.

The first component in Table 28 exhibits high negative loadings from Si and Na, with high postive loadings from Fe, Al, Cr, Zn, V, P and Ni, and explains 66.6 % of the variance contained in the correlation matrix. Component 2, accounting for 20.4 % of the variance, has high positive loadings (>0.5) from Cu, Co, Cr, Zn, V, P, K and a fairly high negative loading from Si. The elements loading heavily on Component 3 (7.4 % of the variance) are Pb, Mn, Mg, with only Sr having a significant loading on the Component 4 (5.5 % of the variance).

The analysis of the trace element data only (Table 29) produced three significant components with Cu, Co, Cr, Zn, V, Mo, P and Ni loading heavily on Component 1, Pb and Mn loading on Component 2 and only Sr loading on Component 3. These components describe 70.2, 21.4 and 8.4 % of the variance in the correlation matrix.

The PCA results using the major element data only produced two significant components (Table 30). Component 1 described 79.5 % of the correlation matrix variance and had high positive loadings from Fe and Al, with high negative loadings from Na and Si. The remaining 20.5 % of the variance is described by Component 2 which has high positive loadings from K and Ti.

The relationships between positive and negative loadings of the individual elements suggests that the data variance is related to the tetrahedral and octahedral composition of the individual minerals. The high weightings of some of the minor

Table 28. Factor matrices calculated for the chemical compositional variables of the clay separates of the major Soil Units of the study region.

	Principal Component Matrix			
	Factor 1	Factor 2	Factor 3	Factor 4
Cu	0.68		0.53	
Co	0.49	-0.41		
B	0.44			
Cr	0.94			
Pb		0.53		
Zn	0.89			
Mn		0.71		
V	0.84	-0.48		
Sr		-0.44	0.65	-0.50
Mo	0.75			
P	0.78	-0.40		
Na	-0.70			
K	0.54	-0.56		0.35
Mg	0.35	0.40		0.35
Fe	0.91	0.30		
Al	0.92			
Ni	0.79			
Ti		0.75		
Si	-0.90			
Eigenvalue	9.34	2.86	1.04	0.78
% variance	66.6	20.4	7.4	5.5

	Varimax	Rotated	Matrix	
Cu		0.53	0.50	0.42
Co		0.61		
B	0.29	0.32		
Cr	0.83	0.52		
Pb			0.55	
Zn	0.64	0.52	0.36	
Mn			0.74	
V	0.68	0.62		
Sr				0.76
Mo	0.76			
P	0.59	0.57		
Na	-0.79			
K		0.81		
Mg		0.61		
Fe	0.89		0.34	
Al	0.89	0.32		
Ni	0.79			
Ti		0.75		
Si	-0.90			

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Table 29. Factor matrices calculated for the minor element levels of the clay separates of major Soil Units of the study region.

	Principal Component Matrix		
	Factor 1	Factor 2	Factor 3
Cu	0.70		0.35
Co	0.55		
B	0.40		
Cr	0.93		-0.27
Pb		0.62	
Zn	0.88		
Mn		0.75	
V	0.91	-0.39	
Sr			0.59
Mo	0.68	0.34	
P	0.85		
Ni	0.80		
Eigenvalue	5.32	1.62	0.64
% variance	70.2	21.4	8.4

	Varimax	Rotated	Matrix
Cu	0.55	0.38	0.50
Co	0.55		
B	0.41		
Cr	0.98		
Pb		0.63	
Zn	0.83	0.31	
Mn		0.75	
V	0.92	-0.30	
Sr			0.66
Mo	0.67	0.39	
P	0.81		0.30
Ni	0.70		0.35

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Table 30. Factor matrices calculated for the major elemental levels of the clay separates of the four major Soil Units.

	Principal Component Matrix		
	Factor 1	Factor 2	Factor 3
Na	-0.79		
K	0.36	-0.68	
Si	-0.90		
Mg	0.36		0.55
Fe	0.95		
Al	0.97		
Ti	0.47	0.63	
Eigenvalue	3.74	0.97	0.44
% variance	72.6	18.8	8.6

	Varimax Rotated Matrix		
Na	-0.84		
K		0.75	
Si	-0.81	-0.31	-0.29
Mg	0.90		0.32
Fe	0.93		
Al	0.42	-0.50	0.43
Ti	0.42	-0.51	0.43

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elements with Fe and Al indicates that these may be substituting in the octahedral layer or occurring in amorphous phases, whereas the loading of Sr independently suggests no direct relationship with mineralogical variation. The association of other minor elements with K suggests a structural relationship with the detrital micas.

Additional analyses were completed to examine the above suggested mineralogical relationships in more detail. Surface area data was included in these analyses in an attempt to discern minor and major element relationships in the smectite component of the clay separates (Table 31). These results are depicted qualitatively in perspective plots by representing the Varimax rotated components in vector space (Figures 43,44,45). The positions of the factor loadings (Table 31) are represented in relation to three factor axes (Stephens, 1976). The projection simulates perspective by use of circles to represent each individual variable, and by decreasing the radius of the circles with distance from the near quadrant. The circles representing the variables with three negative loadings (ie. below the horizontal plane) are solid. Each variable vector would be a unit vector if the represented vector space contained all the numeric information of the initial correlation matrix (Table 21).

The vector diagrams indicate definite relationships between different elements and the SA (surface area) vector which are interpreted as describing chemical associations within the smectite mineral species. The relationships with the K vector indicate compositional parameters of the micaceous component, which is detrital and inherited from the Precambrian Shield lithologies. The Mg vector may be related to the variability of either chlorite or magnesian montmorillonite through the study area.

The groupings illustrated in the vector diagrams are summarised individually below:

1. Figure 43

   Group 1: Fe, Al, SA.

   Group 2: Si, Na.

   Group 3: K.

   Group 4: Mg.

This last elements are isolated in vector space.

Table 31. Varimax rotated matrices calculated for the chemical compositional variables of the clay separates of the major Soil Units of the study region. These matrices were used to plot the vector diagrams (Figures 43 to 45).

Varimax Rotated Matrix

	Factor 1	Factor 2	Factor 3
Minor Elements and Surface Area			
Cu	0.56	0.33	0.47
Co	0.53	-0.27	0.12
B	0.41	0.18	-0.09
Cr	0.97	-0.10	-0.01
Pb	0.09	0.61	-0.04
Zn	0.86	0.25	0.17
Mn	-0.04	0.75	-0.06
V	0.91	-0.35	0.19
Sr	0.08	-0.15	0.68
Mo	0.69	0.35	-0.01
P	0.81	-0.22	0.28
Ni	0.75	0.27	0.36
S.A.	0.83	0.19	0.19
Major Elements and Surface Area			
Na	-0.91	-0.05	-0.03
K	0.16	0.81	0.07
Mg	0.14	0.05	0.51
Fe	0.84	0.10	0.45
Al	0.83	0.35	0.29
S.A.	0.70	0.28	0.31
Si	-0.74	-0.36	-0.42
Total Elemental Composition and Surface Area			
Cu	0.30	0.53	0.50
Co	0.26	0.62	-0.16
B	0.29	0.32	0.21
Cr	0.83	0.52	-0.04
Pb	0.16	-0.14	0.55
Zn	0.64	0.52	0.36
Mn	0.04	-0.18	0.74
V	0.68	0.62	-0.25
Sr	0.03	0.07	-0.19
Mo	0.76	0.07	-0.19
P	0.59	0.58	-0.14
Na	-0.79	-0.04	-0.15
K	0.20	0.82	-0.19
Mg	0.13	0.25	0.61
Fe	0.89	0.18	0.34
Al	0.89	0.33	0.16
Ni	0.68	0.29	0.24
Ti	0.33	-0.24	0.67
Si	-0.79	-0.42	-0.22
S.A.	0.77	0.30	0.17

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2. Figure 44

Group 1: Pb, Mn.

Group 2: V, P, Co.

Group 3: SA, Zn, Ni, Cu, Ti.

Group 4: Cr.

Group 5: Sr

Group 6: Mo, B.

Cr, being in a position in space intermediate between Groups 2 and 3, may be related to both these groups. Ti, though in the same quadrant as the Group 3 elements, is near to Sr in hyperspace and may thus be mineralogically associated with this element.

The most complex vector plot of the three is that depicting the 21 variables in vector space (Figure 45). However the groupings obtained for the variables can be explained logically in terms of ionic substitution within the mineral structures, and may thus be related to provenance of the various mineral species. The arrangement in vector space can be related in the following groups.

3. Figure 45

Group 1:

a) SA, Fe, Al, Mo, Ni, Zn.

b) Cu,B.

c) Mg.

Group 2:

a) Cr, V, P.

b) Co, K.

Group 3: Mn, Pb, Ti.

Group 4: Si, Na.

Group 5: Sr.

The associations in Groups 1 and 2 obviously relate to smectite and mica variations within the correlation matrix, and thus within the study region. Co-ordination number and ionic radii data of the various elements aid in interpreting the actual interrelationships of these elements within the crystal lattice. The radii limiting substitution in the octahedral layers of secondary minerals are 0.41 – 0.73 A°, although MacKenzie (1965) found that a radius

of 0.85 A^0 was the upper limit for fixation in the 6 co-ordinated positions in montmorillonite. This means that Co, Cr, Cu, Mo, Ni and Ti may be present in the octahedral layers of the clays of this study. Mn, in the +4 valance state, may also exist in 6-fold coordination. K and Sr, because of their large ionic radii, could only occur within the interlayer positions of micaceous minerals and Na is probably associated with them. Pb and Mn (+2) are likely related to oxides of weathering products, although it has been suggested that Pb (+2) may proxy for K in micas (Andersson, 1979; Taylor, 1965).

The strong association of Mo, Ni, Zn, and possibly Cu, with SA indicates that these elements must, by virtue of their ionic properties, primarily be present in the authigenic smectites, with the cations probably being released by the weathering of heavy minerals such as hornblende. Mo (+4) is known to substitute for Fe (+3) in biotite, which has been shown to be weathered from the fine clay fraction of these sediments and thus may provide a source for this element. The large size of the MoO^{4-} anion indicates that it will not substitute for the SiO^{4-} of the tetrahedral layers of the smectites. The space association of B and Mo (Figure 44) suggests that they may be present in the same species. The Mo may also be present in the haematite which is present in highest amounts in the Kinosis and Legend units.

The fact that Cu is on a different plane in space than the other three elements suggests either a different source or location. The source may be either from ferromagnesian or plagioclase minerals (Taylor, 1965). The Cu may be present in the beidellitic species of the smectite group, which has been previously suggested to weather from feldspars. The location of Cu in vector space, however, may also relate its occurence to the magnesian chlorites known to be present in the samples, or indicate that it is replacing Mg in the octahedral layer of the smectite minerals. All four elements (Cu, Mo, Ni, Zn) have been described as occurring in significant amounts in smectite minerals (Weaver and Pollard, 1973) and are present in highest amounts in the clays from the Legend unit which tends to confirm their association with the authigenic rather than the primary minerals.

The location of B in space (Figure 44) indicates a relationship with the smectites. B has been reported to be concentrated in marine sediments where the BO_4^{5-} probably replaces the SiO_4^{5-} tetrahedra of the clay minerals (Taylor, 1965), and high B contents

(>100 ug gm^{-1}) have been suggested to indicate marine origin of shales (Potter *et al*, 1962). B has been reported to have higher levels in fine than coarse clays (Taylor, 1965). The source of the B could also be the plagoiclase minerals which have been shown to be relatively highly weathered in the soils of Alberta (Abder-Ruhman, 1980).

Group 2 (Figure 45) indicates the relationship of Cr, Co, V and P with the micaceous component of the clay separates. The first three elements (Cr, Co, V) are problably substituted in the octahedral layer of these minerals. The enrichment of V in the Legend samples, and its association with P, suggests a possible complex formation with Fe or Al in these samples, perhaps as a coating on the hydrous mica component of the sediments (Weaver and Pollard, 1973; Norrish, 1975)

The position of Sr in space indicates a relationship with the micas which is not apparent from the initial PCA, although Taylor (1965) suggests that Sr does not enter the K positions of micas readily , probably because its smaller size requires 8-fold coordination rather than the 12-fold coordination of K. Thus the vector isolation (Figure 44, 45) may represent a random occurrence in the micas. The fact that the highest Sr concentrations are in the Legend unit suggests that it may be fixed in the "wedge" sites of the hydrous micas described for these samples, having weathered from K-feldspars.

Ti is closely related to Sr in Figure 44 and Mn, Pb in Figure 45. The substitution for Fe (+3) in biotites (Taylor, 1965) may explain the first association, and the second association suggests the presence of possible minor amounts of rutile (TiO_2) and pyrolusite (MnO_2). The latter has been described as a weathering product common in sediments. Pb (+2), which has similar mean levels in all units, is similar in size to K (+1) and Ca (+2) and thus may come from minerals such as micas and feldspars (Dudas and Pawluk, 1980). The lack of any spatial relationship of Pb with any element except Mn indicates presence as oxides or sulphides in the clay separates. The Pb ions having been released during weathering of feldspar minerals where it occurs as minor sulphide inclusions (Taylor, 1965).

Mn oxides have been reported to contain up to several thousand ug gm^{-1} of Pb (LaRiche and Weir, 1966; Taylor and MacKenzie, 1966), and Pb has been found in Fe and Al phosphate minerals in high amounts (Norrish, 1968). Although complex Mn secondary minerals may contain significant amounts of minor elements (Norrish, 1975), the low

correlation coefficients between Mn and elements such as Co, Ni and Pb suggests that this may not be the case in these soil parent materials.

The association of Fe and Al with SA in these diagrams implies that the regional variability of these elements is related to smectite variability. This spatial association confirms the regional variation of the nontronite and beidellite species within the smectite group. Unfortunately further separation of the clays, perhaps on the basis of magnetic susceptibility, would be necessary to further define the association of specific minor elements with the mineral phases in the soil materials.

The association of Si and Na is confusing. It may indicate that Na content varies inversely to that of K in the micas, as Na is known to replace K in interlayer positions. The relative isolation of Mg in hyperspace indicates that variability of this element, though related to substitution in magnesian smectites, may also reflect the varying levels of chlorite described in the discussion of the clay mineralogical variation in these sediments.

The correlation matrix was analysed using Cluster Analysis, with the CLUSTAN series of programs (Wishart, 1975). The resultant classification diagrams (Figures 46,47,48) show somewhat similar groupings to those obtained by PCA but are difficult to explain in mineralogic terms because K,SA, Fe and Al, which were used as mineral species indentifiers, are in the same groups. The loss of the apparent third dimension thus tends to limit the application of this technique for the mineralogic interpretation of the chemical data.

7.2.4 Conclusion.

The application of PCA to the chemical compositional data of the clay separates was found to reduce the complexity of the interrelationships of the correlation matrix. The variation in minor element content appeared to be related to the mineralogic varition between the soil units. Analysis of the rotated component matrix by means of vector diagrams showed that Cu, Ni, Mo and Zn were probably associated with the octahedral layers of the authigenic smectite minerals, wheras the Cr, V, Co and P were related to the micaceous minerals. Variations in Mn and Pb content within the samples were thought to be related to either X-ray amorphous oxides, oxy-hydroxides, or to sulphides in the clay separates.

7.2.5 Cluster Analysis of Clay Separates:

The Application of discriminant analysis earlier in this section demonstrated that, using all the analysed chemical variables, separation into groups based on the mapped till units was accurate no more than 90% of the time if all sample variance was to be explained.Thus cluster analyses of these same variables were done to clarify the grouping of these soil clay separates.Several analytical stratagies were chosen:

1. The factor scores output using all the chemical data from the factor analyses presented above were used as input into a cluster analysis,using the CLUSTAN statistical package of programs (Wishart, 1975). This has the advantage of reducing the number of variables to be used in calculating the distance function. Dendrograms were produced by hierarchical clustering using furthest neighbour,group average,centroid and Ward's method similarity coefficients (Webster, 1977) based on the squared Euclidian distance coefficient to produce the initial correlation matrix.
2. Minor element compositions of the clays were analysed.
3. Major element compositions of the clays were analysed.

The dendrograms displayed (Figures 49,50,51) were produced using Ward's method of hierarchical fusion as it is considered to be the best of the hierarchical classification options (Wishart, 1975; Webster, 1977).

The objective of classification analysis in a data set such as has been generated during the various stages of this study is not to actually prove the subjective classification developed for the map units described in the field, but rather to produce groupings which are based on the similarity of individuals and to examine these groupings to determine which processes or factors may be controlling group separations. These group separations may be based on compositional differences which bear no direct relationship to field occurrence. The hierarchical cluster technique employed essentially produces a Q-mode analysis in which intersample relationships are used to produce the final classification.

The dendrograms utilising factor scores as input variables (Figure 49) describe an objective classification of individual clay separate samples. The groups (I - IV) selected by the four classification methods were essentially similar, with reallocation of only one

or two samples being obtained by the different techniques. Thus only the dendrogram produced by Ward's method is presented (Figure 49). The majority of the samples from the Legend unit are quite distinct, being classified into a distinct group in each case. The samples classified into other groups (39, 36, 38) are all from the southeast of the area mapped as Legend where the dynamics of glacial flow could have been conducive to deposition of material of Shield provenace. The Dover system also represents a fairly independent group, probably reflecting the sedimentation of kaolinitic and micaceous minerals in the proglacial Lake McConnell, with the finer smectite clays being removed by meltwater on the breaching of the ice dams to the northeast. The presence of Horse River and Kinosis samples in the same groups reflects the similarities in clay mineralogical compostion of these two tills, even though one is calcareous and the other is not.

The analyses (Ward's Method) based on minor element composition produced three major groups (Figure 50):

Group I. This was dominated by lacustrine clay separates.

Group II. This was dominated by separates from the Legend unit.

Group III. This was composed of clay separates from the Kinosis and Horse River soil units.

Group III reflects the provenance similarity of the materials comprising the Kinosis and Horse River units, with Group II reflecting the difference in provence of the Legend unit materials. The occurrence of the lacustrine samples as an independent cohesive unit supports the suggestion above that minerals enriched in the major discriminating elements were washed from the lacustrine basin during drainage. The finer size of the smectite floccules, in conjunction with their physicochemical properties, would have been sufficient for them to remain in in suspension and thus be removed during basin drainage. The groups defined using only major element composition of the clay separates (Figure 51) tends to support the classification based on minor elements, but the group separations are not as well defined with overlaps appearing between the separates from the Kinosis, Horse River and Dover units. There are even samples of the Legend unit in a sub-group with samples of Shield provenance. This supports the discriminant analysis results which suggested that a regional classification of till materials based on the major element chemistry of the clay separates may not produce a differentiation which

can be related to geologic unit or actual physiographic variation.

Application of hierarchical classification techniques to analysis of clay separate compositional variables produced a series of objective groups. Comparison of these groups with those obtained by field mapping illustrated the compositional similarity of the clays from two of the four mapped units. The Kinosis and Horse River units obviously have a similar composition and, thus, provenance. The classification separates the Legend and Dover samples into individual units, reflecting their compositional differences from the other two units.If the regional location of the group members of the numerical classification is delineated on a map, the general pattern reflects that based on the intuitive field–based classification. Thus the clay separate compositional variation produced a numerically based classification which can be related to variations in material provenance and subsequent glaciogenic processes.

8. MINERALOGY OF THE SAND FRACTION.

The mineralogy of the sand fraction was examined by petrographic , X-ray diffraction and total dissolution (Pawluk, 1967) techniques. The fine sand fraction (50 - 250 um.)was studied in the greatest detail as it has been described as the terminal grain size of glacial comminution (Dreimanis and Vagners, 1971). The objective of this discussion is further characterisation of the geochemical and mineralogical properties of the major Soil Units of the study area. This section will, in part, respond to the suggestion raised by Abder-Ruhman (1980) that the Cretaceous and Shield lithologies contribute different mineralogic components to the feldspar suite found in soils further south of the present study area.

8.1 Sand Mineralogy of the Major Soil Units

The fine sand mineralogical composition as summarised in Table 32 is based on analyses of specific gravity separates. The heavy mineral fraction displays no significant differences between the Soil Units. Petrographic examination of selected thin sections of this separate displayed no qualitative differences in mineralogical composition. The suite was dominated by approximately equal quantities of amphiboles, biotite, opaque minerals, iron oxides and altered minerals, with lesser quantities of garnets and pyroxenes. These relative amounts are similar to those reported in other studies of parent materials in Alberta (Abder-Ruhman, 1980; Howitt, 1981; Twardy, 1969).

The data describing light mineral composition is based on the total dissolution of the < 2.75 specific gravity separates. The contents of Ca, K and Na in these separates were allocated to the end-members of the feldspar compositional series (Ca to anorthite, K to orthoclase and Na to albite). The balance was assigned to quartz.

Quartz is the dominant light mineral in all the Soil Units, K- and Na-feldspar are second in overall abundance while Ca-feldspars are fourth in abundance. There is no significant difference in the quartz content of the Dover and Kinosis Units whereas the Horse River and Legend Units have contents significantly different from each other and from the other two. The Horse River Unit has the lowest quartz content and the Dover and Kinosis Units the highest.

Table 32. Modal sand mineralogical composition of the fine sand separates of the major Soil Units in the study region.

	DOVER	KINOSIS	HORSE RIVER	LEGEND	REGION
	Mineralogical	Composition	(%)		
Heavy Minerals	1.74 a	1.58 a	1.77 a	2.10 a	1.80
Quartz	89.22 c	89.24 c	83.31 a	86.83 b	87.15
K-feldspar	3.54 a	3.85 a	5.36 b	5.10 b	4.46
Na-feldspar	3.30 a	4.15 a	5.89 b	4.70 ab	4.51
Ca-feldspar	2.21 b	1.19 a	3.66 c	1.26 a	2.08
Na- + Ca-feldspar	5.51 a	5.34 a	9.55 b	5.96 a	6.59

Elements followed by the same letter are not significantly different at the 0.05 level based on Duncan's New Multiple Range Test.

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The contents of K-feldspar in both the Dover and Kinosis Units are similar based on Duncan's New Multiple Range Test, as are the Horse River and Legend Units. The mean content of this feldspar ranges from 3.54 % in the Dover Unit to 5.36 % in the Horse River Unit. These levels are similar to those reported in other studies of northern Alberta soils (Lavkulich et al, 1964), but slightly lower than those from southern Alberta (Abder-Ruhman, 1980; Twardy et al, 1974).

Na-feldspar contents display a different distribution among the Soil Units, with the Horse River Unit having a significantly different mean content of this mineral (5.89 %) when compared with the other three units, although there is overlap with the Legend unit. Ca-feldspar contents display a similar pattern. The pattern for Na-feldspar demonstrates that the Kinosis and Legend units have have statistically similar contents (1.19 and 1.26 % respectively), whereas the Dover (2.21 %) and Horse River units are significantly higher in content of this mineral group. If the mean levels of these two minerals are combined the only unit with a mean content significantly different from the other three at the 0.05 level is the Horse River unit. The absolute levels of this combination on a regional basis is lower than that described by Twardy et al (1974), but similar to that reported for the studies from northwestern Alberta (Lavkulich et al, 1964; Pawluk and Dudas, 1978).

Thus the application of the Duncan's Multiple Range Test to the mineralogical ingredients in the fine sand separates of these Soil Units indicates that it is not generally possible to isolate the individual units on the basis of the mean content of any of the major light mineral species, although in one instance (Ca-feldspar) the Horse River was significantly different in content from the other three. These findings are supported by the data for more southerly till units described by Twardy et al (1974). They also indicate that the suggestion of Abder-Ruhman (1980), that the Cretaceous and Shield lithologies may contribute a different suite of feldspar minerals to the soil materials is not correct in this region. Examination of the surface morphology of the feldspar minerals from the Legend and Kinosis Units demonstrated no apparent variation in the degree of surface weathering in these two units (see examples of weathered grains in Plate 2).

CONCLUSION

This investigation of the mineralogical and geochemical variation of parent materials was undertaken to provide baseline information on the levels of major and minor elements, and on the clay and sand mineralogy of the major parent materials of the region. The absolute elemental levels were correlated with regional textural variation. The modal values documented for regional surficial materials were compared with those recorded in the literature, and sources of variation were discussed in detail.

Levels of all elements determined, with the exception of Ca and Mg, tended to display highest levels in the Legend Soil Unit associated with the Birch Mountains to the northwest of the region. This was shown by both numerical analysis and regional contour maps to be related to the variation in clay content within the region.

Regression analyses, in which minor element levels were the dependent variables and major element levels were the independent, were calculated to determine whether major element levels could be utilised to predict minor element abundance. The "predictor" elements explained a maximum of approximately 90 % of the minor element variance, and a minimum of 45 % in the case of Pb. The most important "predictor" elements selected were Al, Fe and K which confirmed the interpretation of the factor analyses in suggesting that minor element variability is related to clay mineralogical variation. Pb again was the exception, with over 90 % of the explained variance of the regression equation being related to Ti. This indicates that much of the Pb variability in these sediments may be related to occlusion in the weathering products of Fe, or by the variation of the relatively minor amounts of heavy minerals found in this study.

Factor analysis indicated that much of the variance in the trace element levels was associated with ion substitution in the octahedral and tetrahedral layers of the authigenic minerals. This technique indicated a high degree of interrelationship between trace element levels. This interrelationship linked with the variability in Fe, Al and Ti defined some 70 % of the total data variance. This variance was suggested to be related to the variability in clay mineralogy within the region. Another 15 % related to Ca and Mg variability, which must be linked with the presence of calcareous materials and high pH. The remaining variance was explained primarily by Mn (8 %) and Sr (6 %) . The former was related to the presence of manganese nodules observed at some sites, and the latter

possibly reflects mica variability, with the highest Sr levels occurring in the Dover Unit. Subsequent analysis of minor and major elements separately further defined the above general relationships, with variability in micaceous and smectite minerals being implicated in explaining the bulk of the regional chemical variation.

A group of 46 samples representing four major soil units was characterised in detail.Discriminant analysis indicated that As , Cu and Cr were the elements which were able to define 75 % of the discriminant space between the Legend and Kinosis units. This reflects the higher levels of As, Cu, Cr in the Legend unit. Sr was the other element which described much of the variability in discriminant space, and this related to the high levels in the Dover unit in comparison to the other three.

Characterisation of clay separates from these four Soil Units indicated that all were dominated by micaceous minerals, smectites , kaolinite and chlorite, with varying levels of each in the individual units. These mean levels were analysed by DMRT and the significant differences defined at the 95 % confidence level.

Samples of the clay separates from the Legend and Kinosis Units were analysed for ^{18}O content. The levels from the Kinosis unit (13.5 $^{o}/_{oo}$) were similar to those documented for clay minerals in Formations to the north east of the study region, whereas the levels for the Legend Unit (16 – 17 $^{o}/_{oo}$) are the same as those for marine Cretaceous sediments. Thus clay mineralogy of these units was examined in more detail, and the importance of the Cretaceous and Shield provenances to the surficial tills was examined. The Legend unit was found to have a significant component of non-ideal beidellite, whereas that of the Kinosis was ideal. There was no apparent difference between the mica and montmorillonite species in these units, although the kandites do display minor variations. The kaolinite displays disorder in both units, and there is evidence for dickite in the coarse clay separate of the Kinosis Unit.

The chemical composition of the clay separates were analysed in detail by factor analysis to ascertain the location of the individual minor elements in both clay species, and lattice sites within the individual minerals.

The elements B, Cu, Mo, Ni and Zn are probably in the authigenic smectites, and Co, Cr and V are in the micaceous minerals. Mn, Pb and Ti are in the weathering products such as haematite, goethite or X-ray amorphous compounds, whereas Sr appears to

substitute randomly for K in the mica structure.

Discriminant analysis, based on the major soil units, indicated that B, V, Mn and Zn describe most of the inter-unit spatial variability. These elements occur in function which enable classification of individuals into the mapped units, and are again related to sediment provenance as all are known to be enriched in authigenic minerals from marine sediments.

The sand mineralogy displayed marked similarity between all groups, with quartz being the dominant mineral. The contents of Ca-feldspar, K-feldspar and Na-feldspar were similar in all units, although the means were significantly different at the 0.05 level for one or two units in all cases.

In conclusion, the analytical results confirm the initial field separations of parent materials, and provide data on spatial variablity of textural and chemical characteristics within the study region. This chemical variability can be related to substitution within individual mineral species.

FIGURES

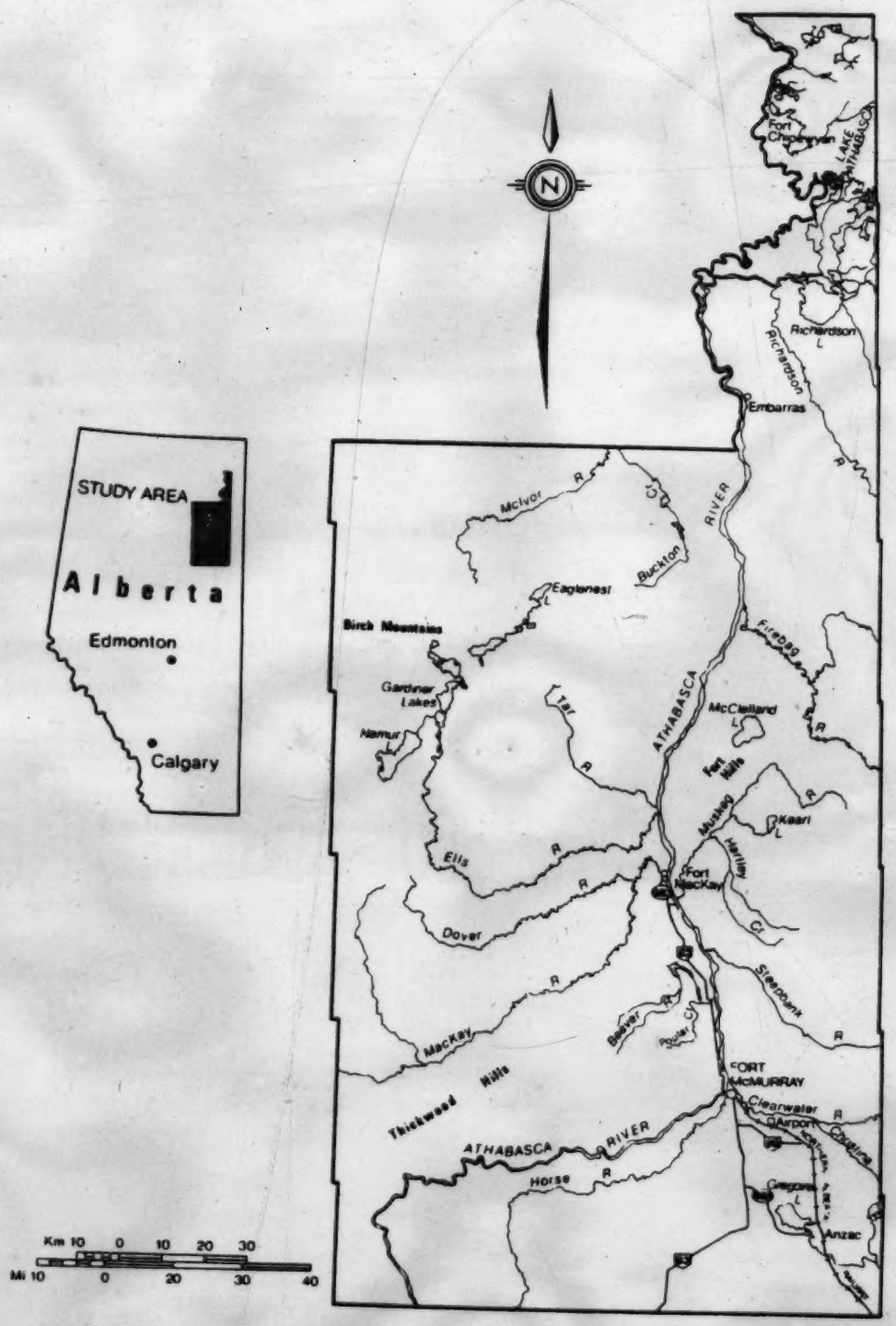

Figure 1. Location of the study area.

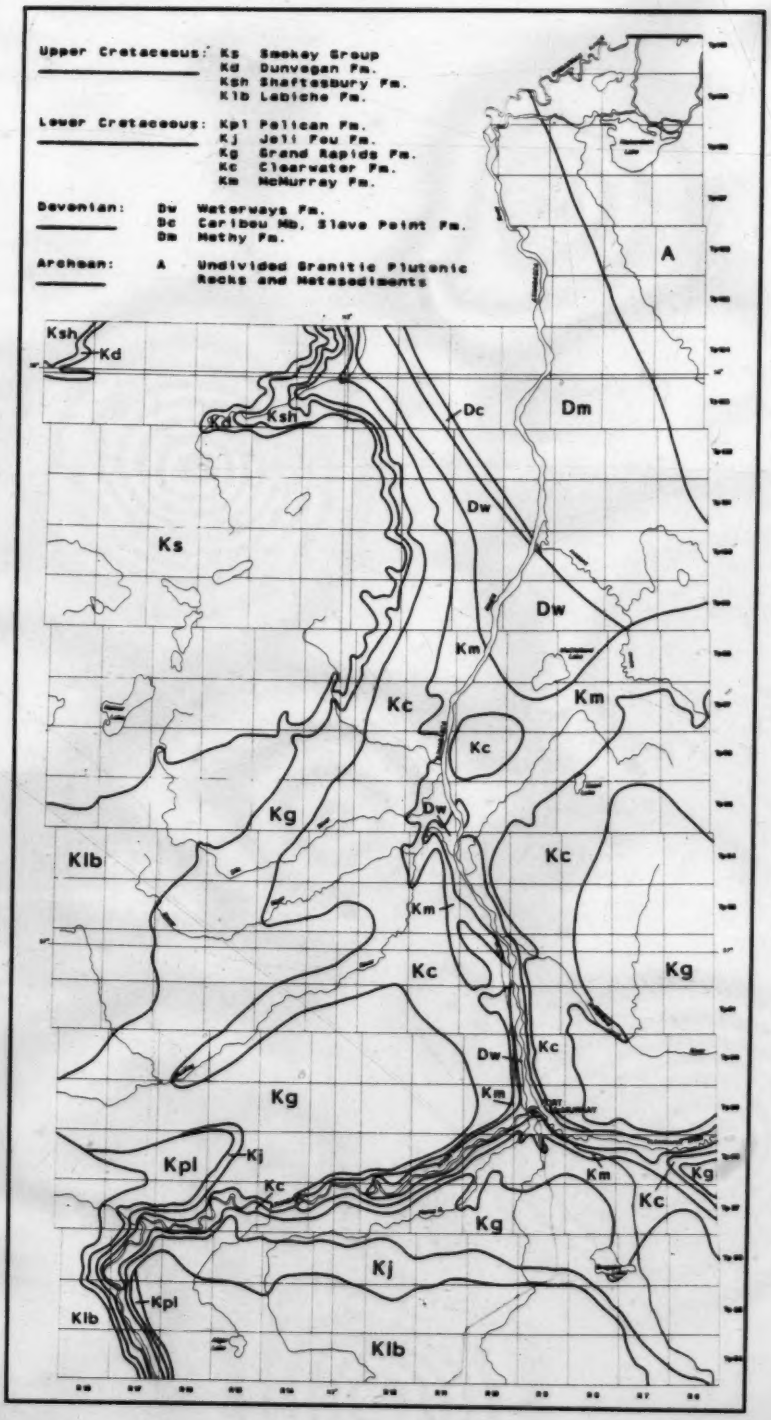

Figure 2. Bedrock geology of the study area.

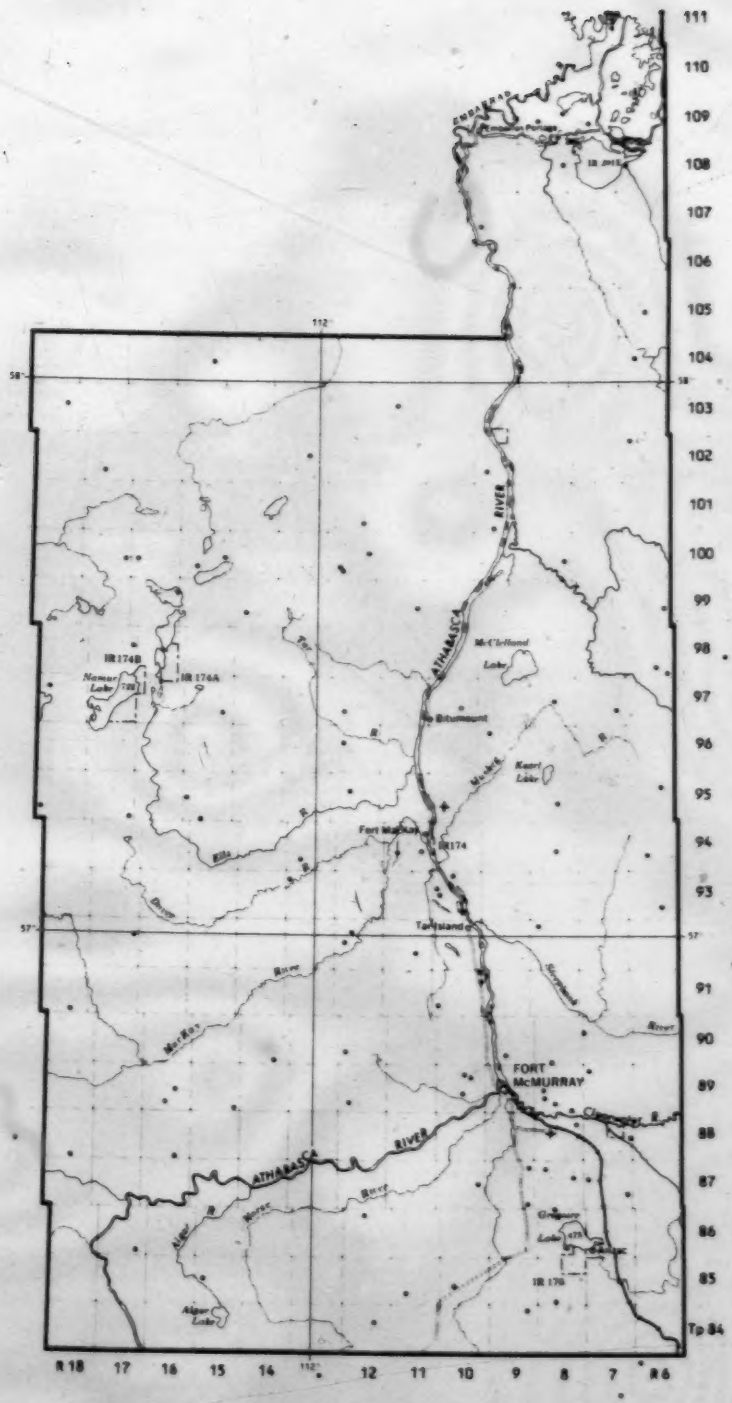

Figure 3. Location of parent material sampling sites within the study area.

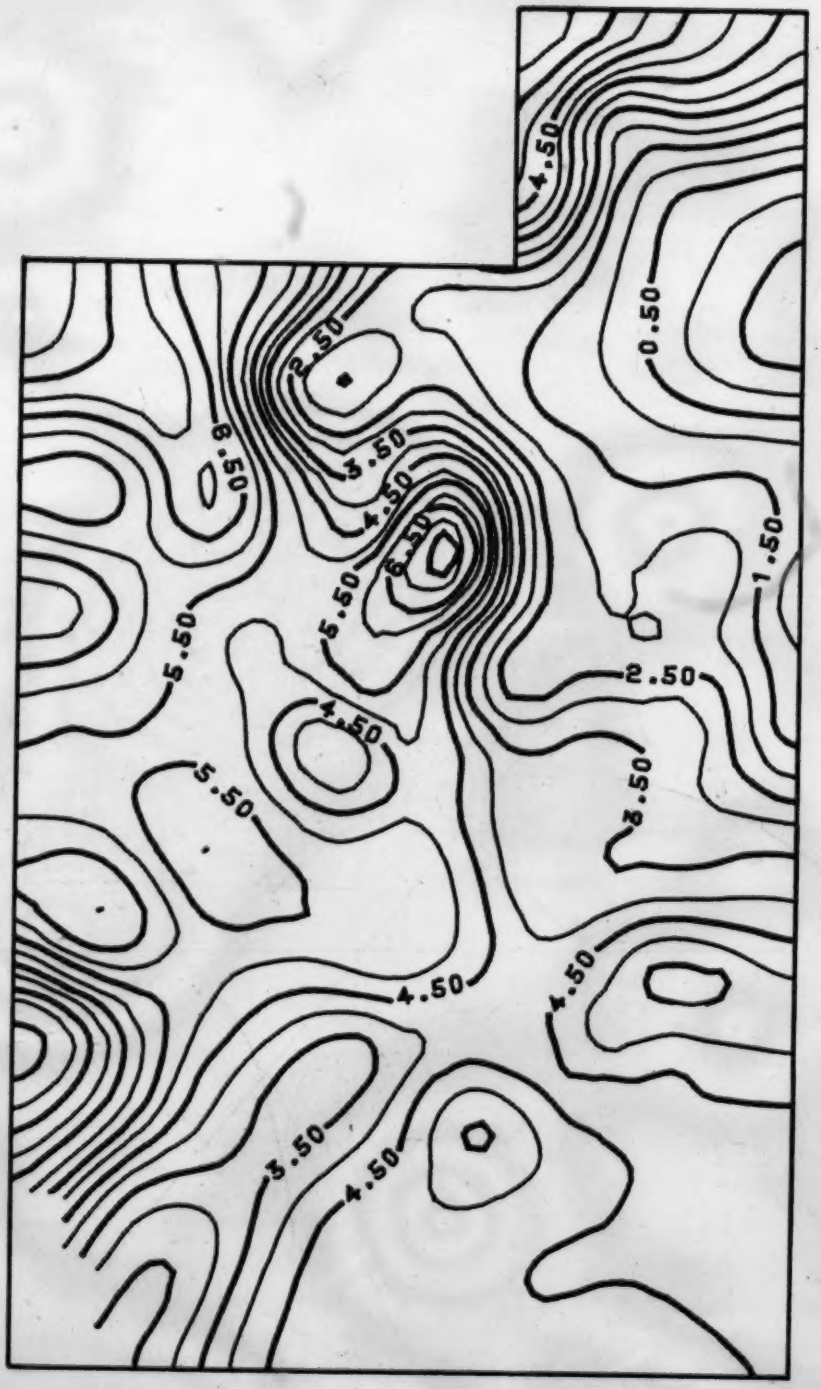

Figure 4. Contour map depicting Al levels (%) in the soil parent materials of the study region.

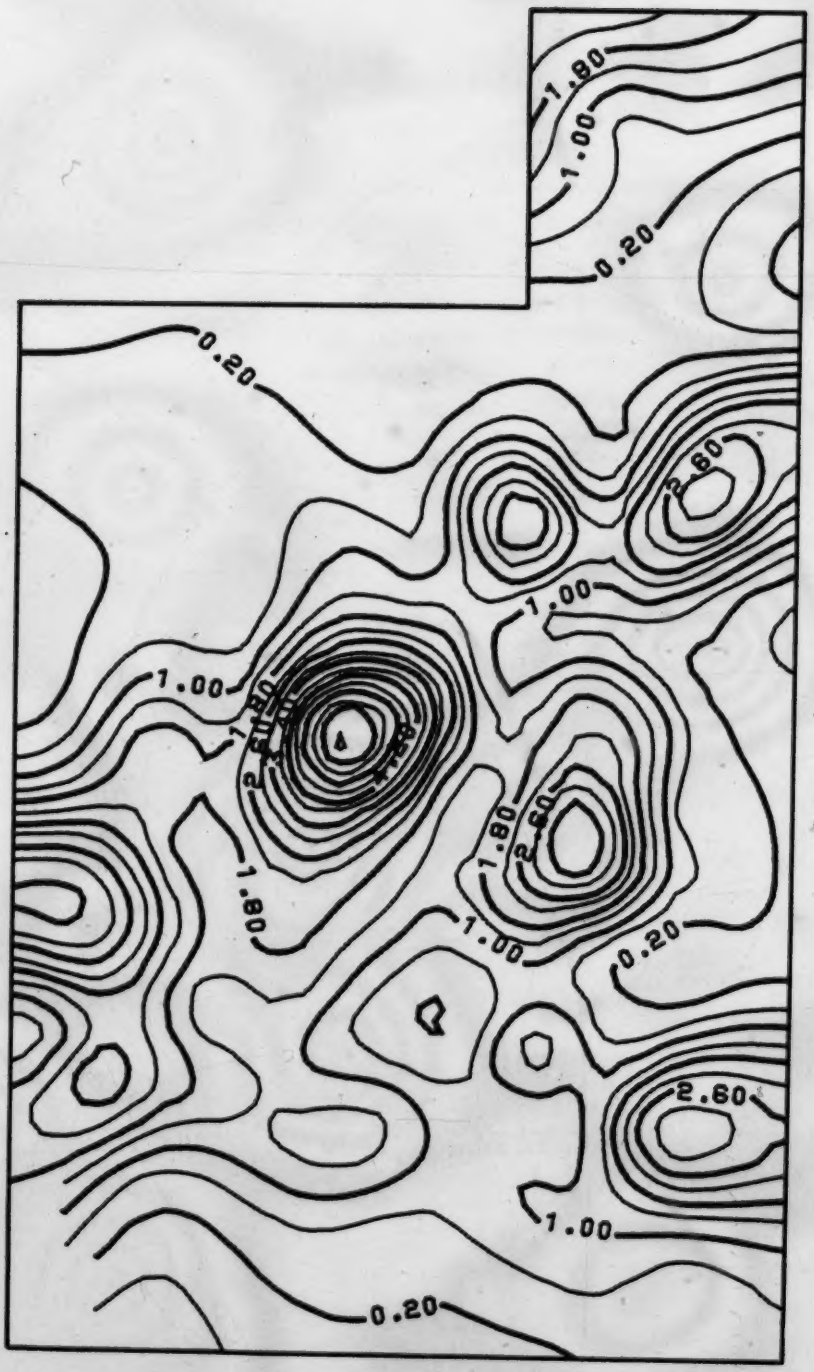

Figure 5. Contour map depicting Ca levels (%) in the soil parent materials of the study region.

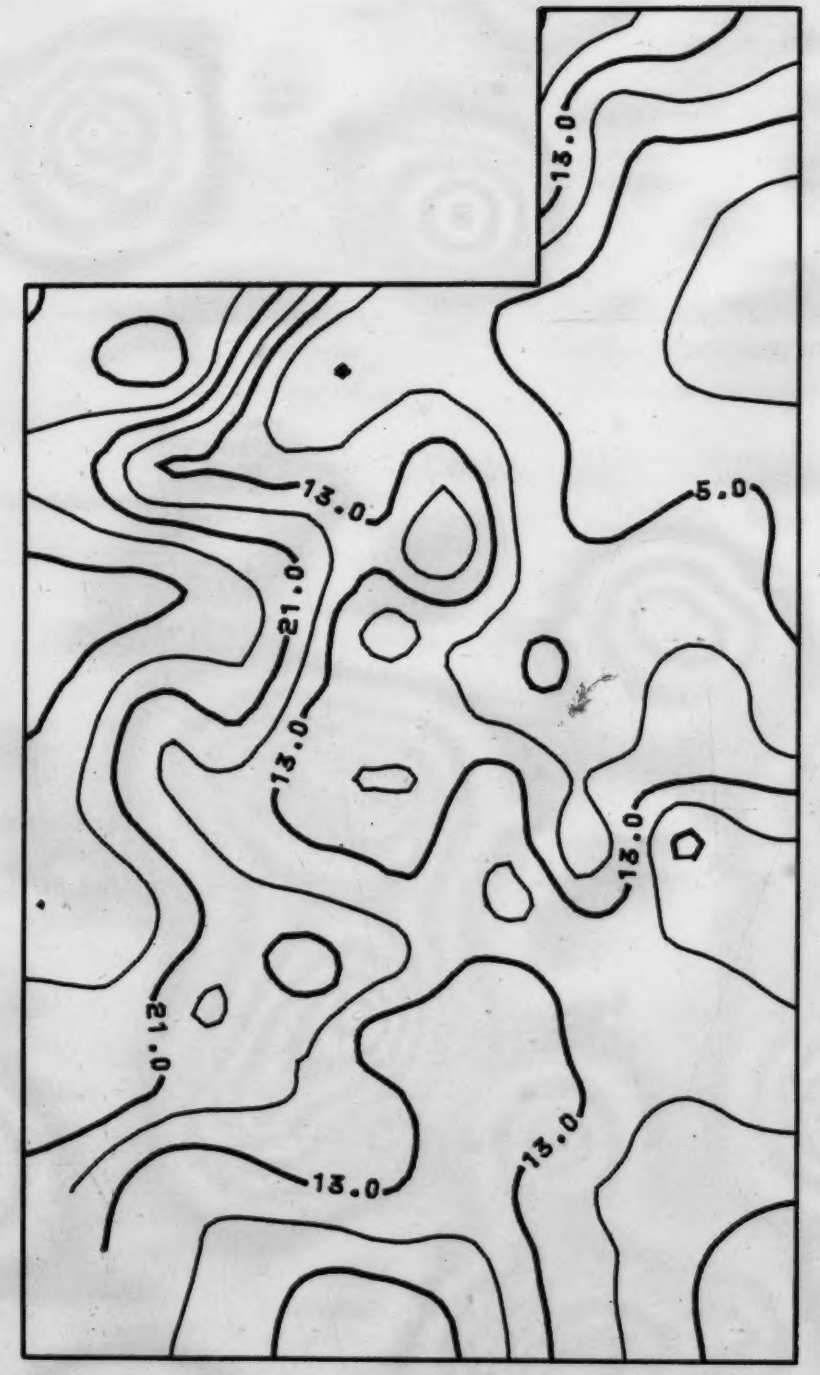

Figure 6. Contour map depicting Co levels (ug gm^{-1}) in the soil parent materials of the study region.

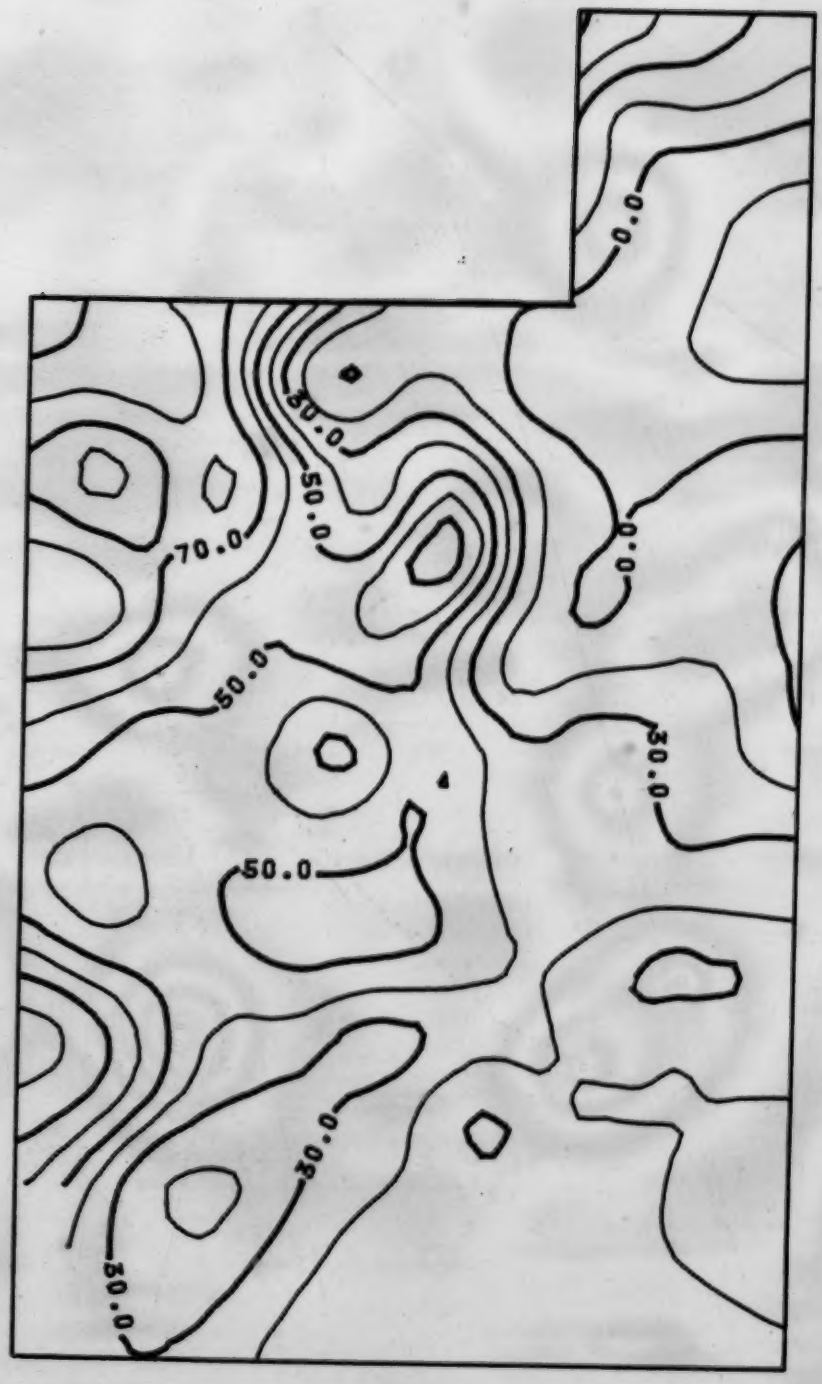

Figure 7. Contour map depicting Cr levels (ug gm^{-1}) in the soil parent materials of the study region.

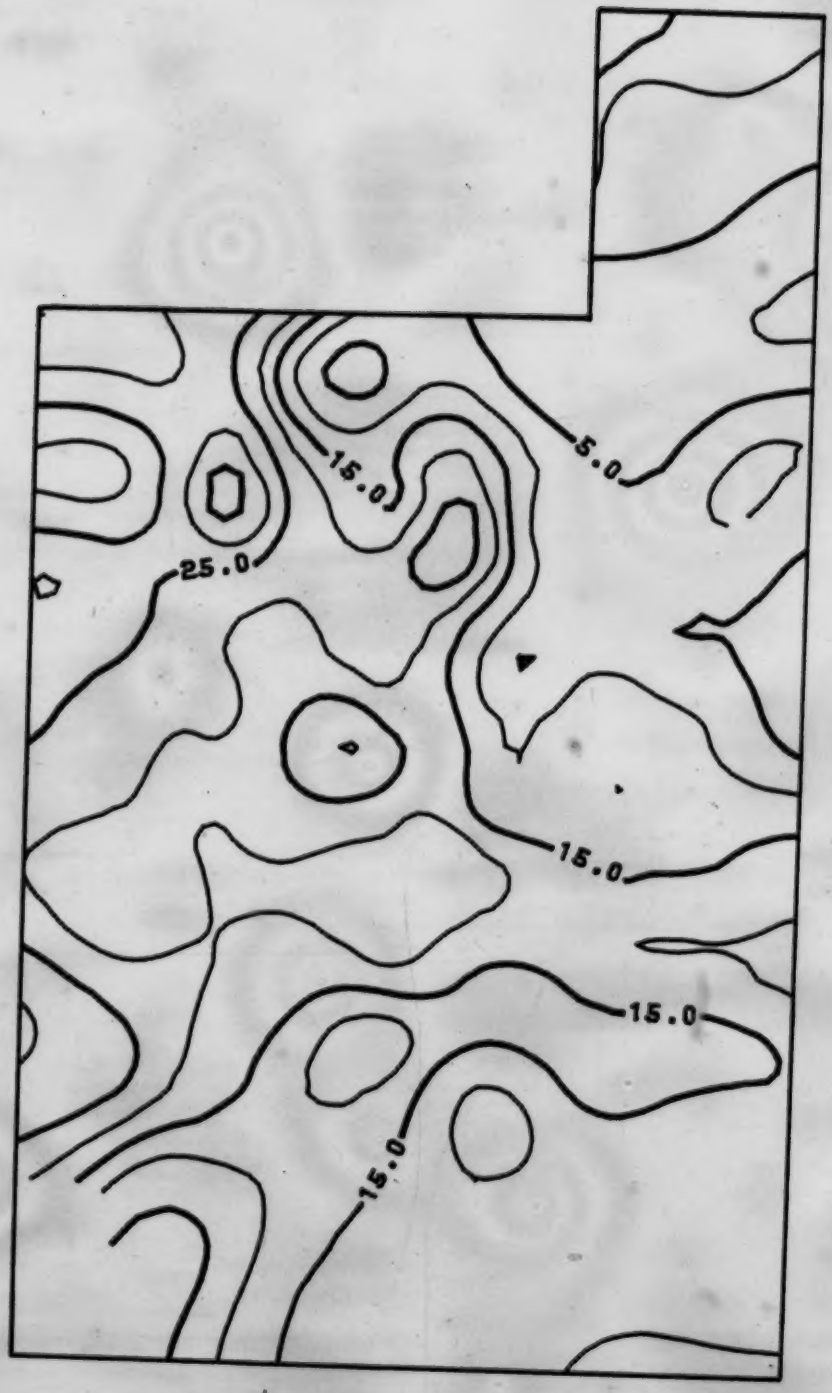

Figure 8. Contour map depicting Cu levels (ug gm^{-1}) in the soil parent materials of the study region.

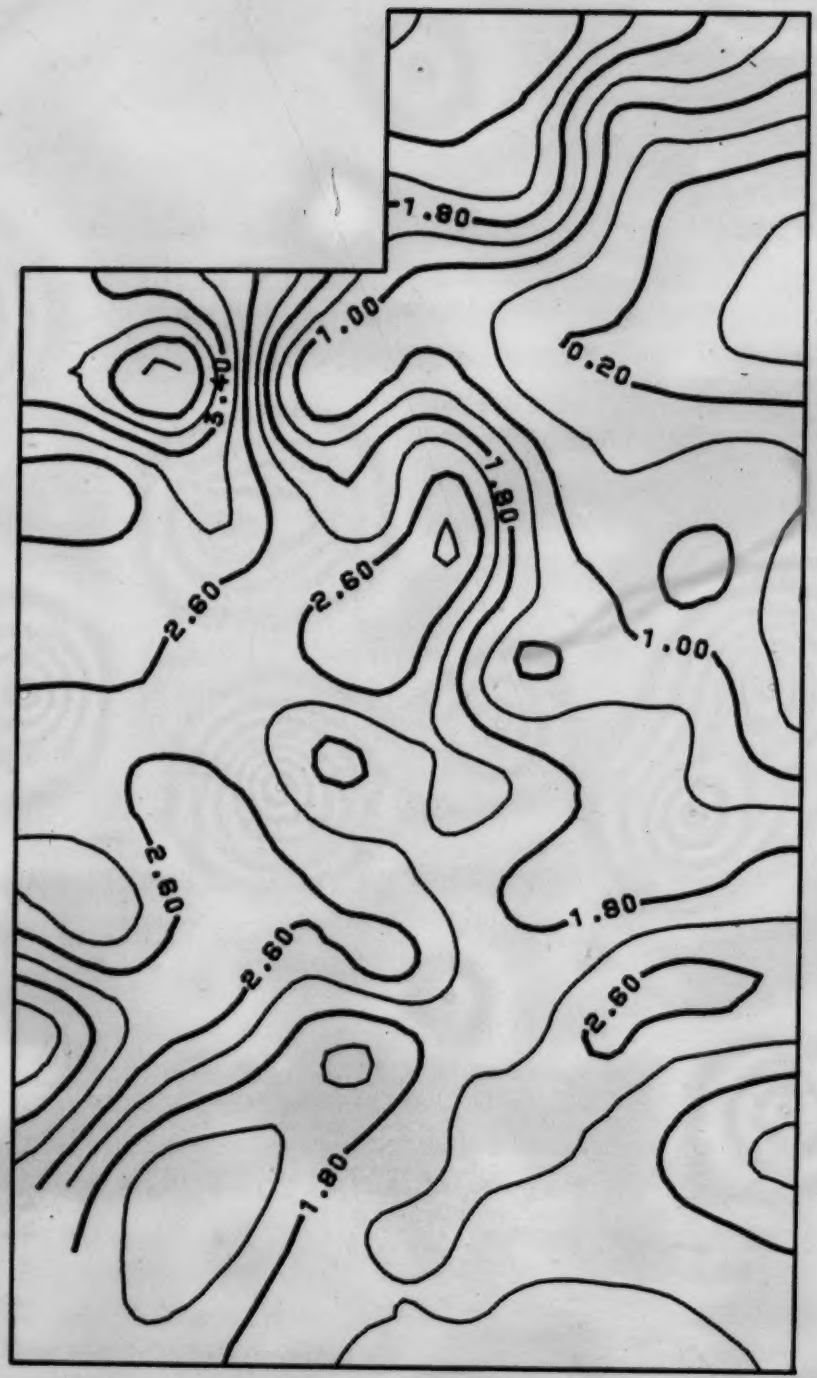

Figure 9. Contour map depicting Fe levels (%) in the soil parent materials of the study region.

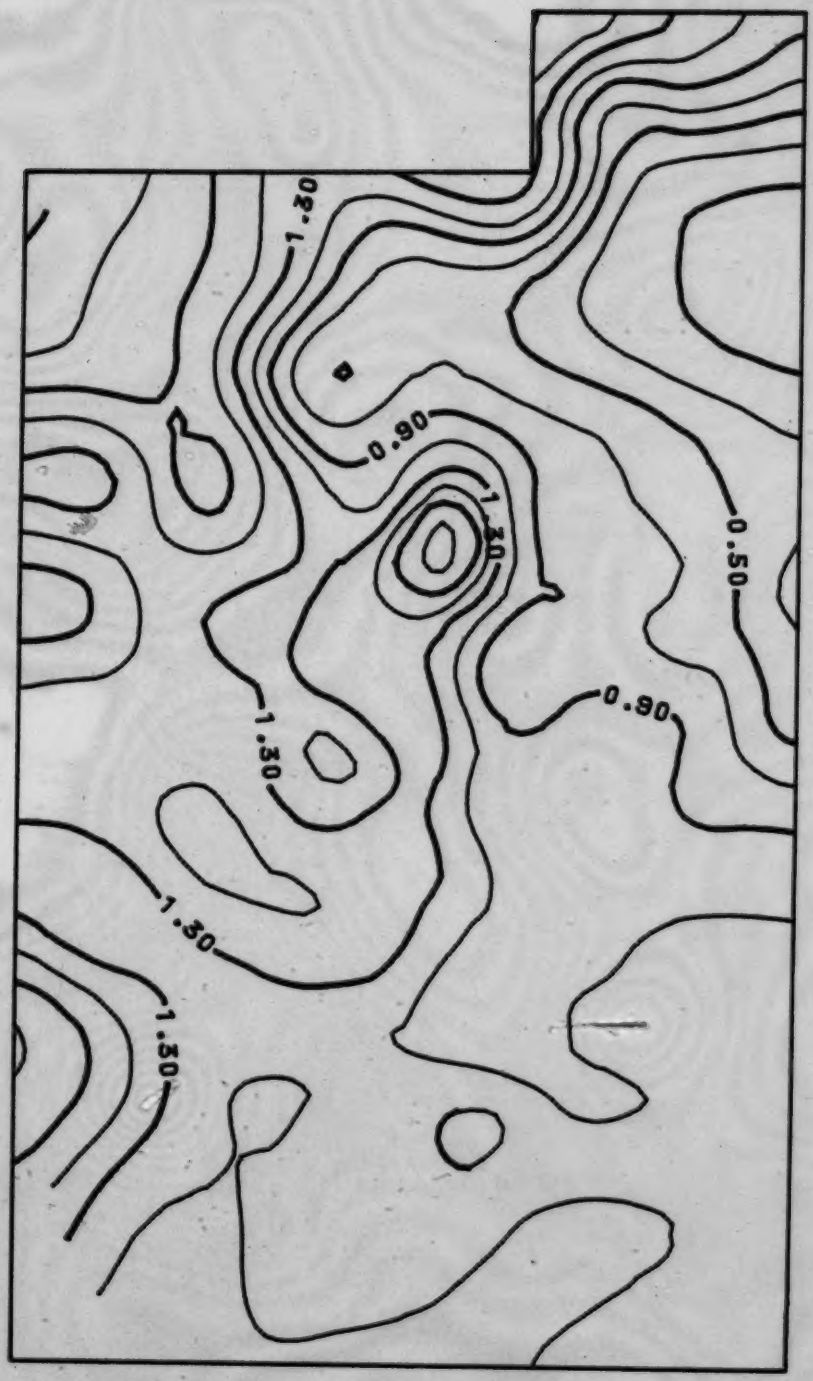

Figure 10. Contour map depicting K levels (%) in the soil parent materials of the study region.

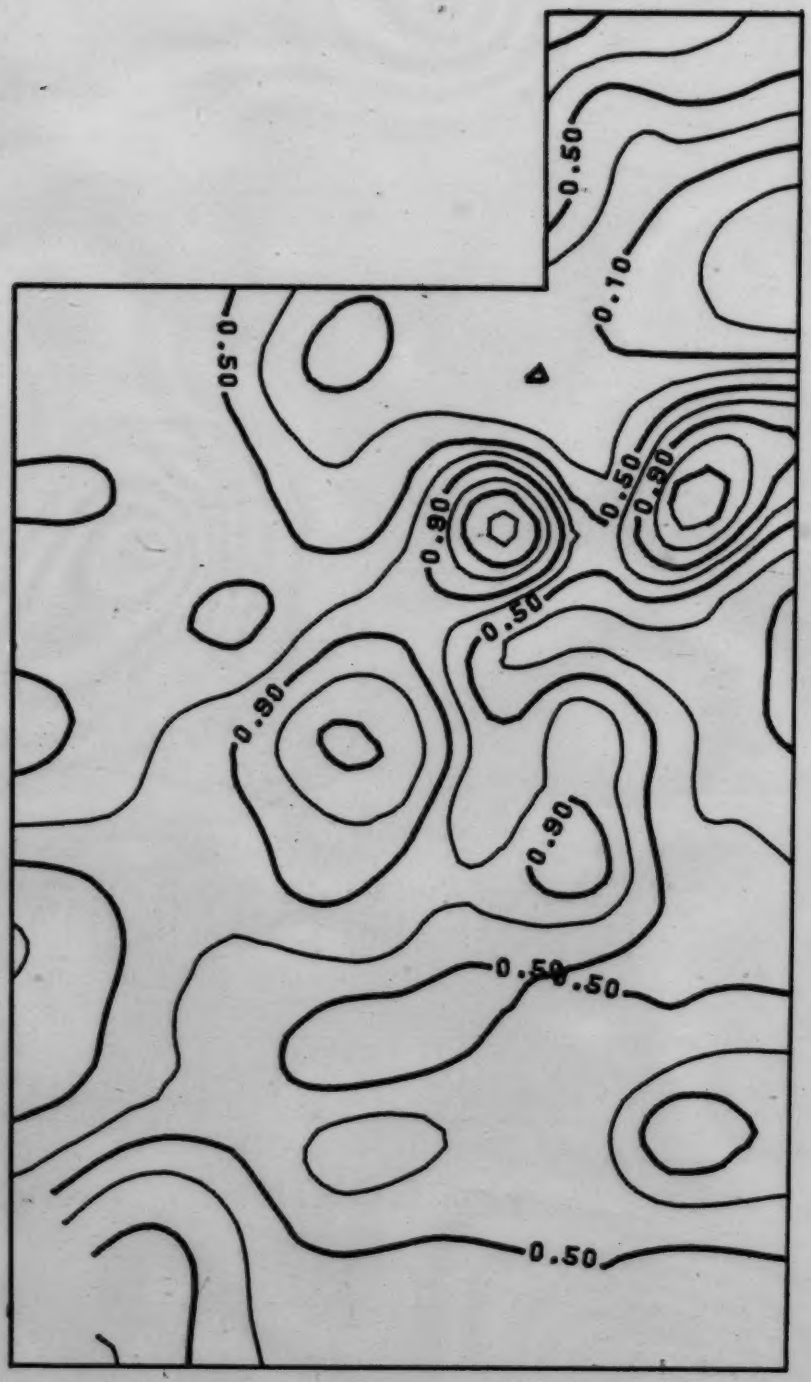

Figure 11. Contour map depicting Mg levels (ug gm^{-1}) in the soil parent materials of the study region.

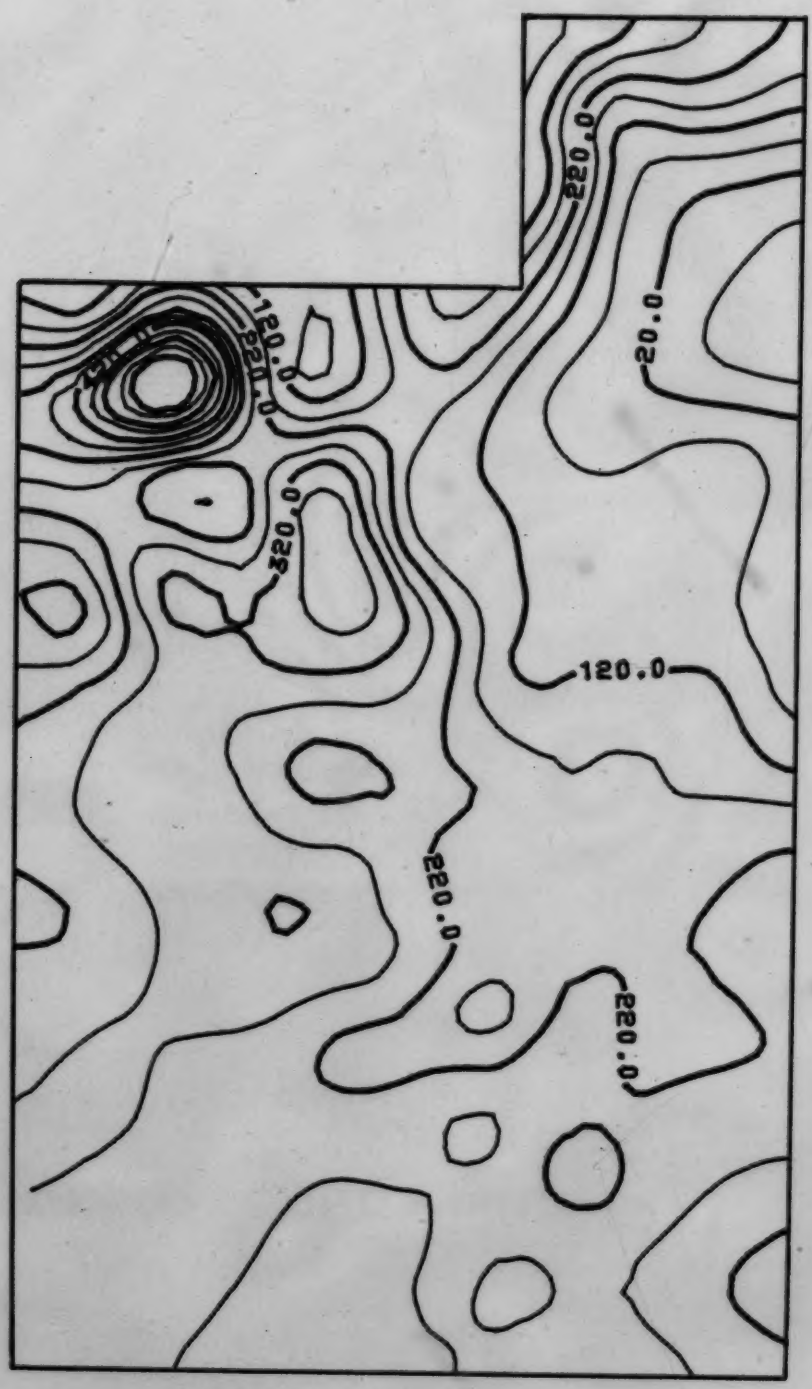

Figure 12. Contour map depicting Mn levels (ug gm^{-1}) in the soil parent materials of the study region.

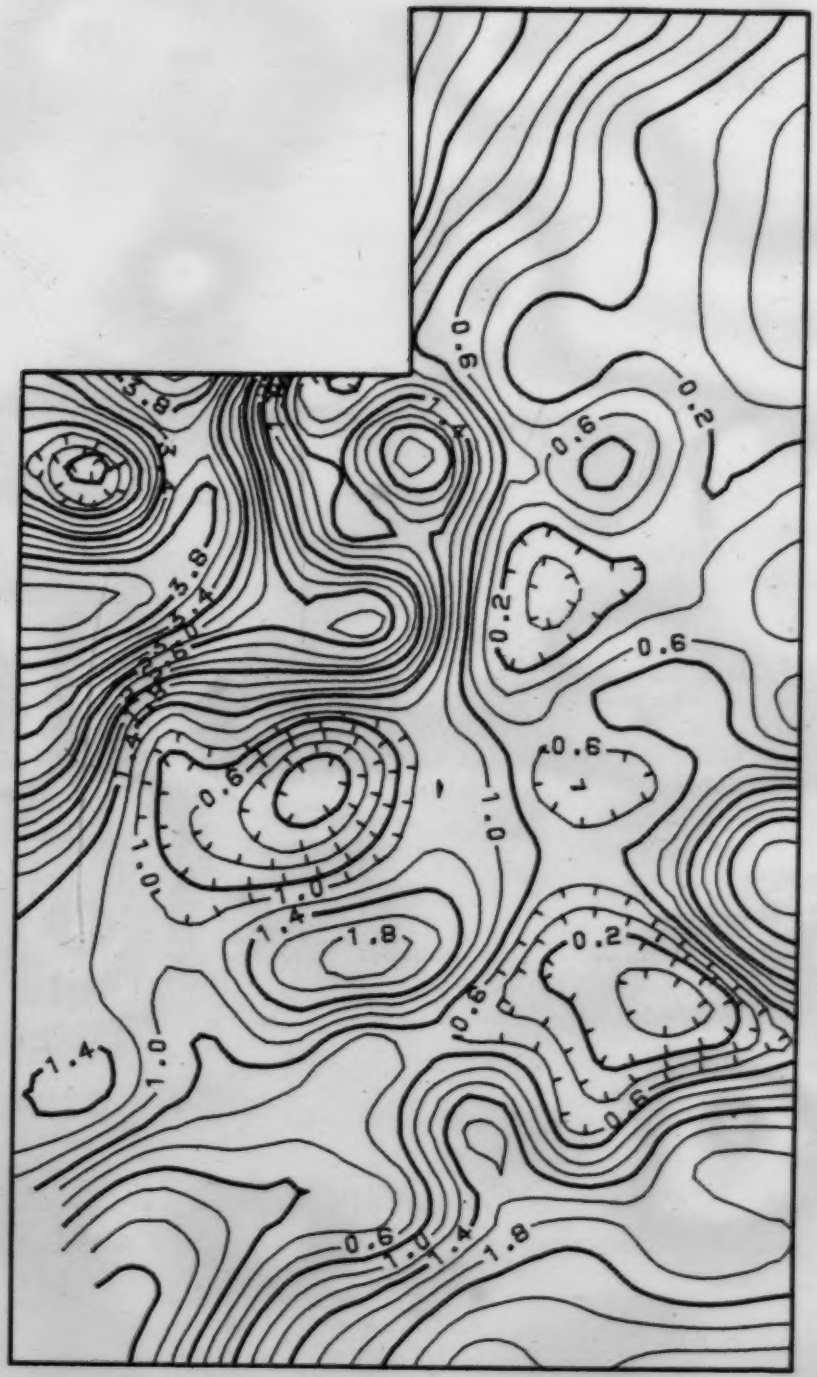

Figure 13. Contour map depicting Mo levels (ug gm^{-1}) in the soil parent materials of the study region.

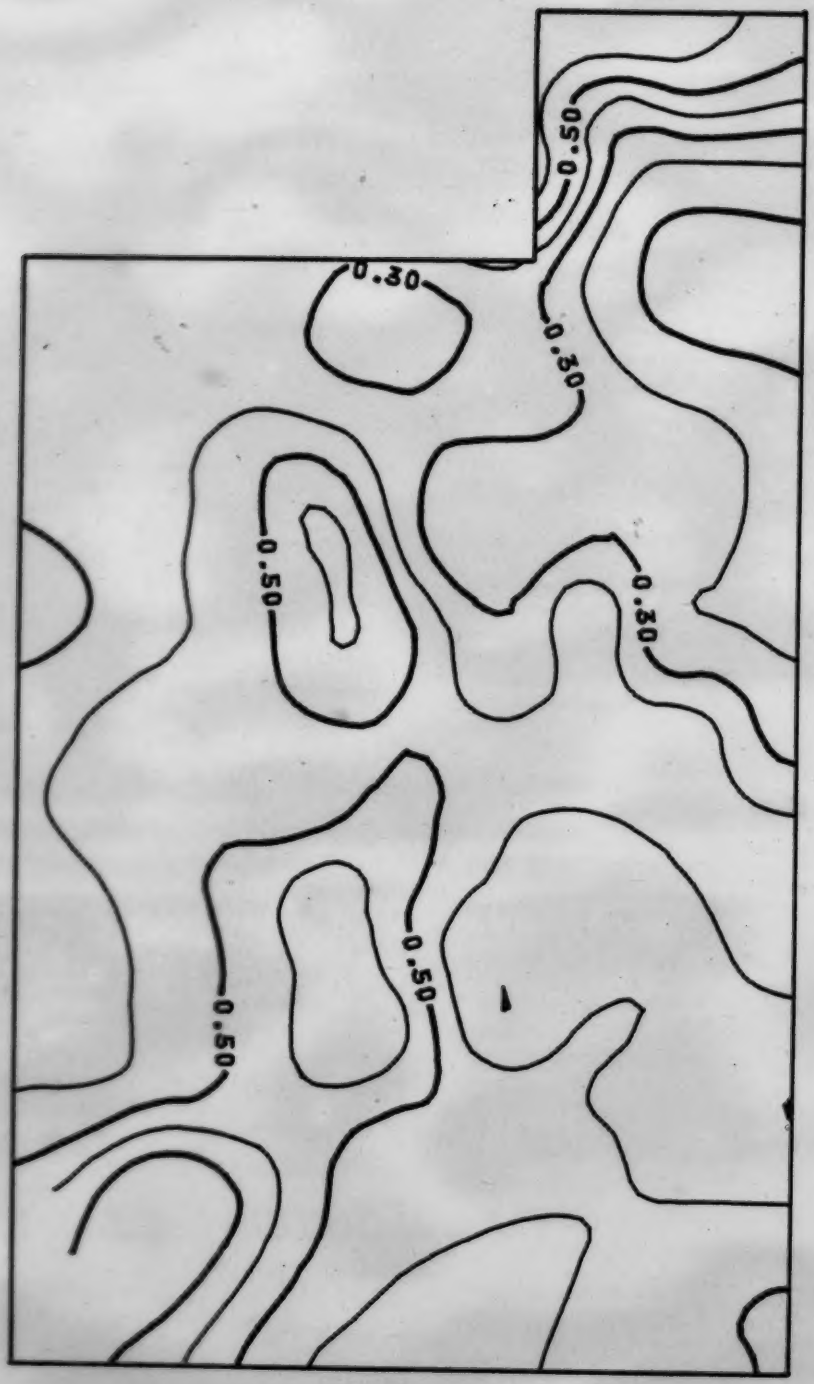

Figure 14. Contour map depicting Na levels (%) in the soil parent materials of the study region.

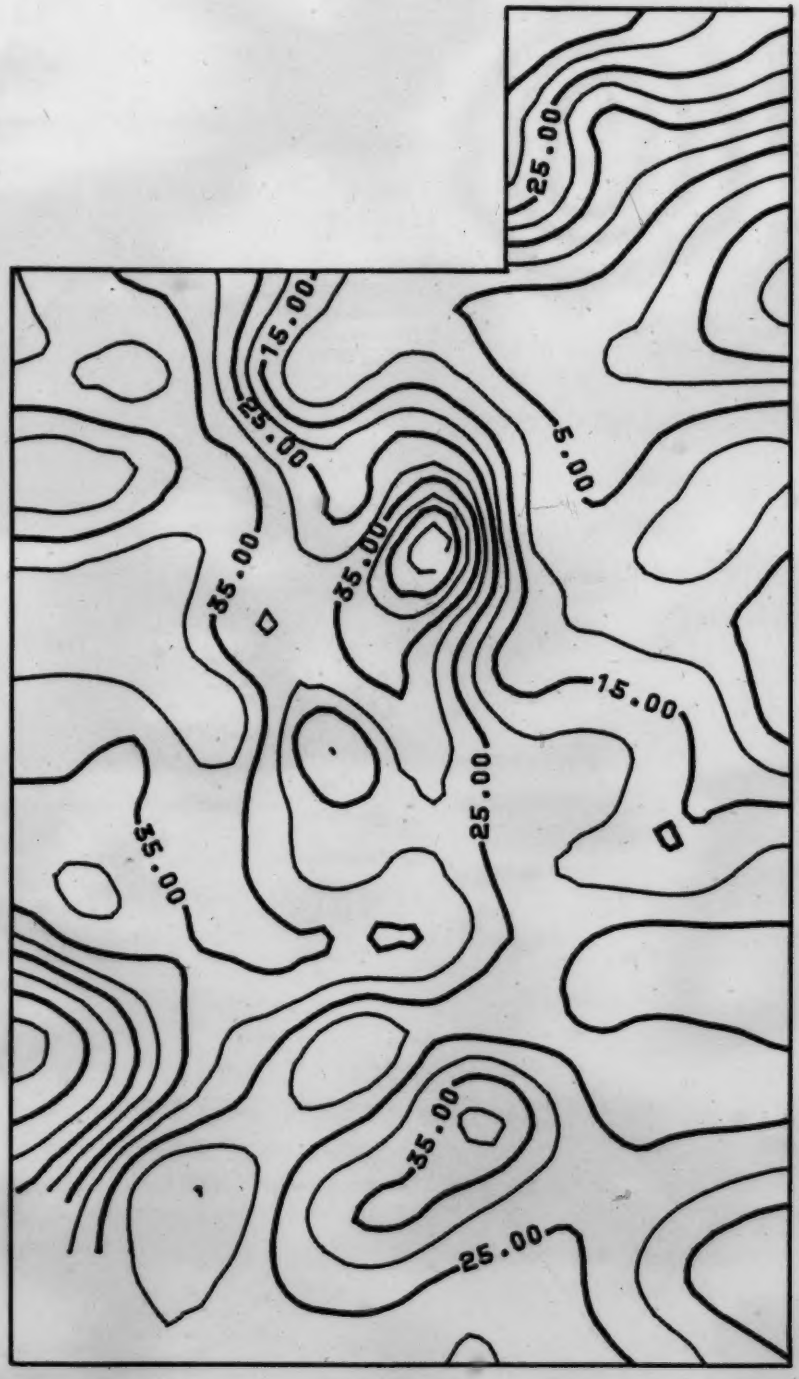

Figure 15. Contour map depicting Ni levels (ug gm^{-1}) in the soil parent materials of the study region.

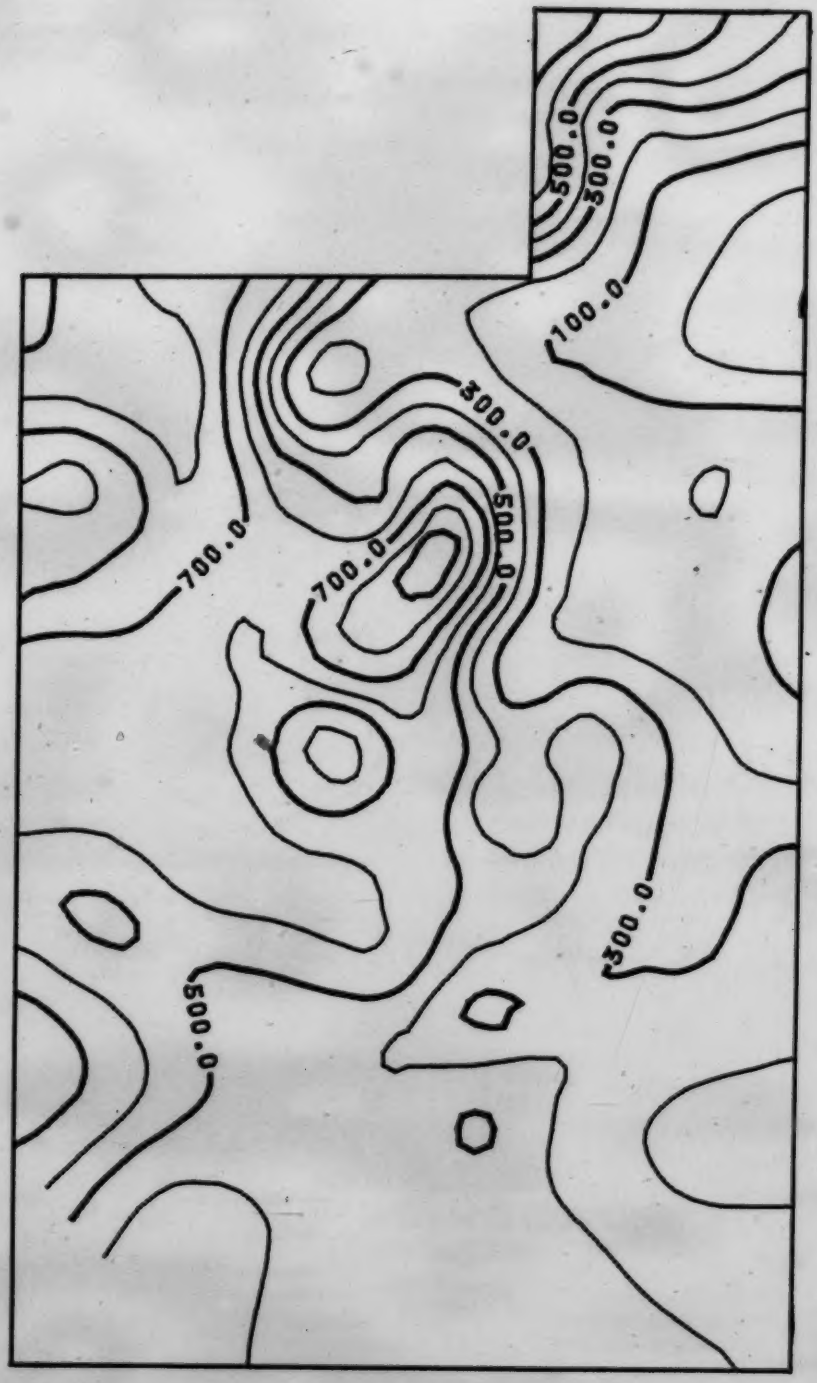

Figure 16. Contour map depicting P levels (ug gm^{-1}) in the soil parent materials of the study region.

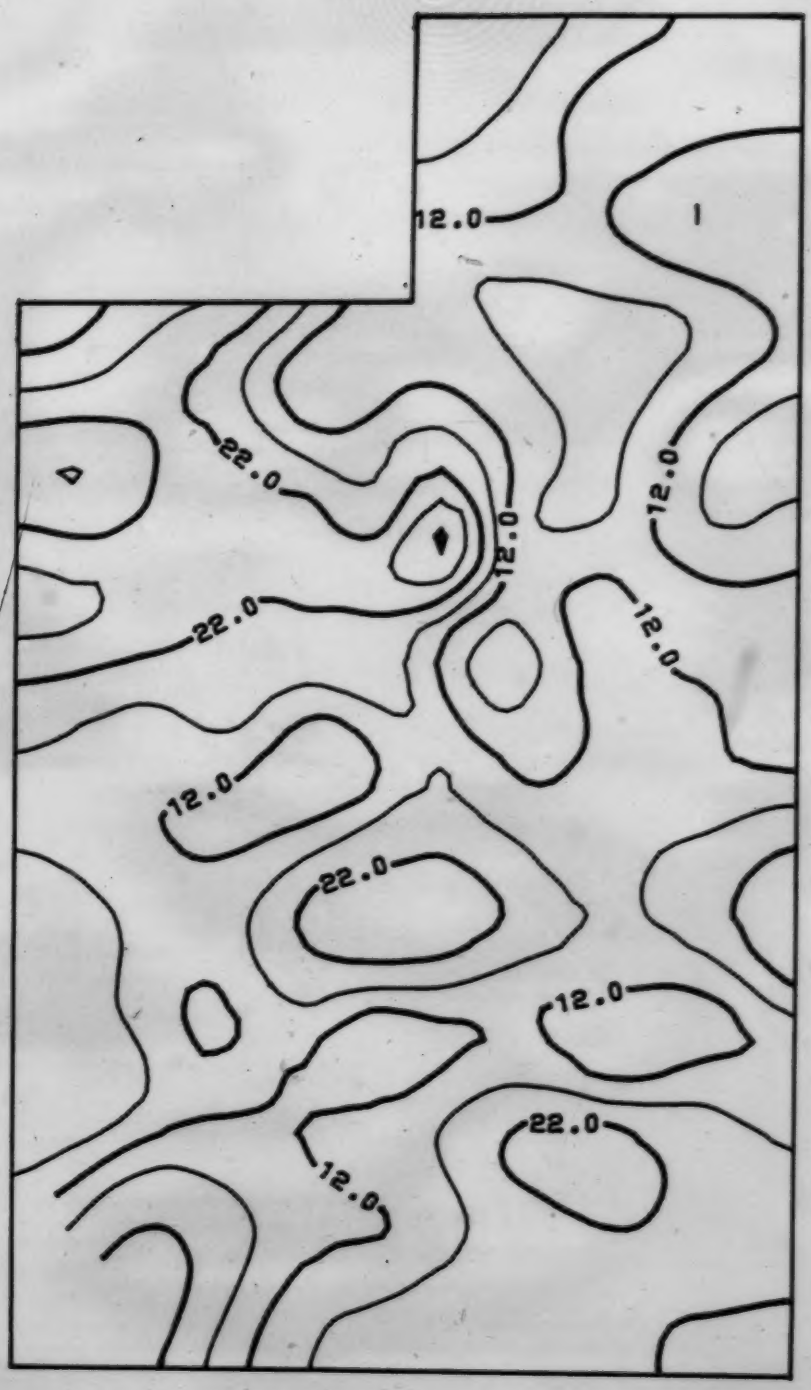

Figure 17. Contour map depicting Pb levels (ug gm^{-1}) in the soil parent materials of the study region.

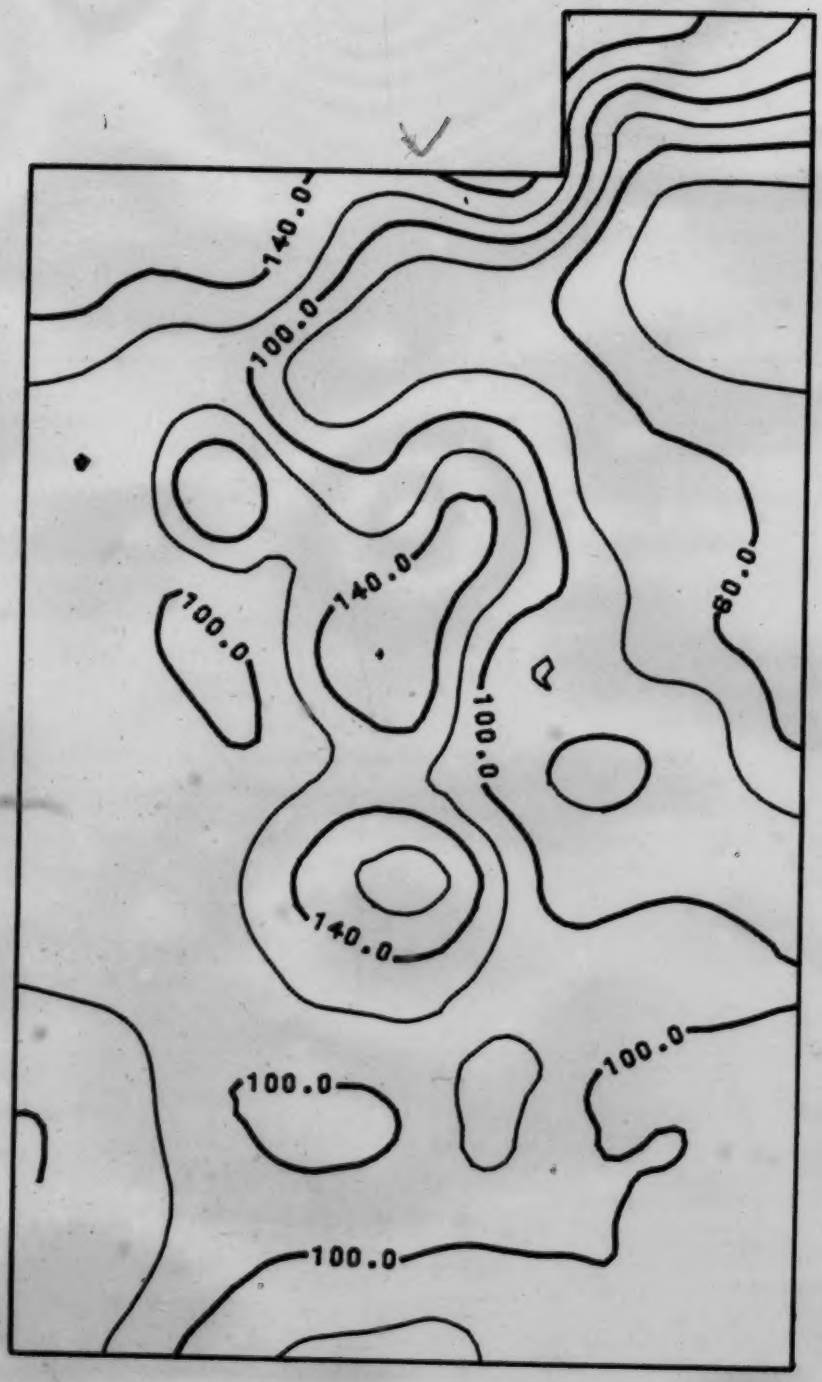

Figure 18. Contour map depicting Sr levels (ug gm^{-1}) in the soil parent materials of the study region.

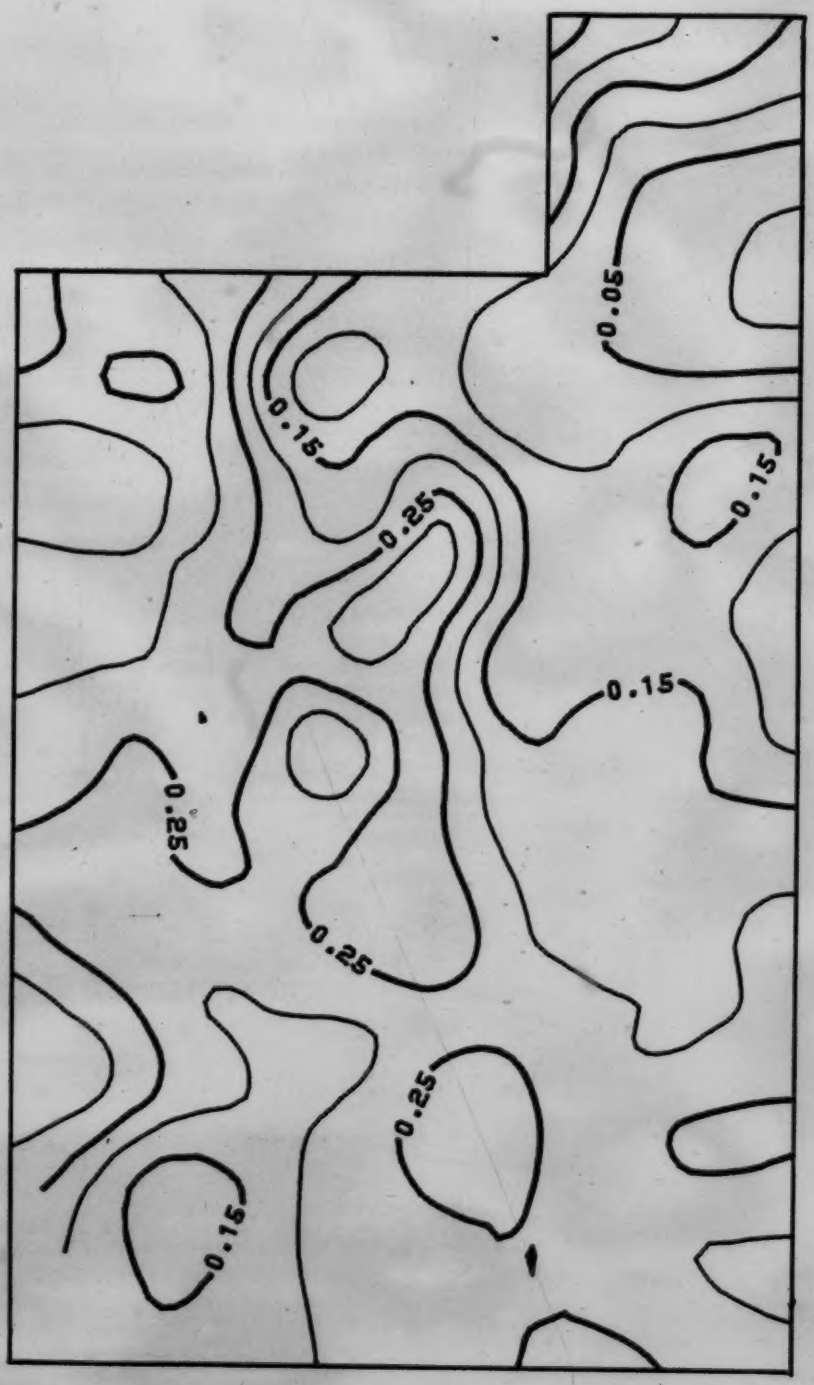

Figure 19. Contour map depicting Ti levels (ug gm^{-1}) in the soil parent materials of the study region.

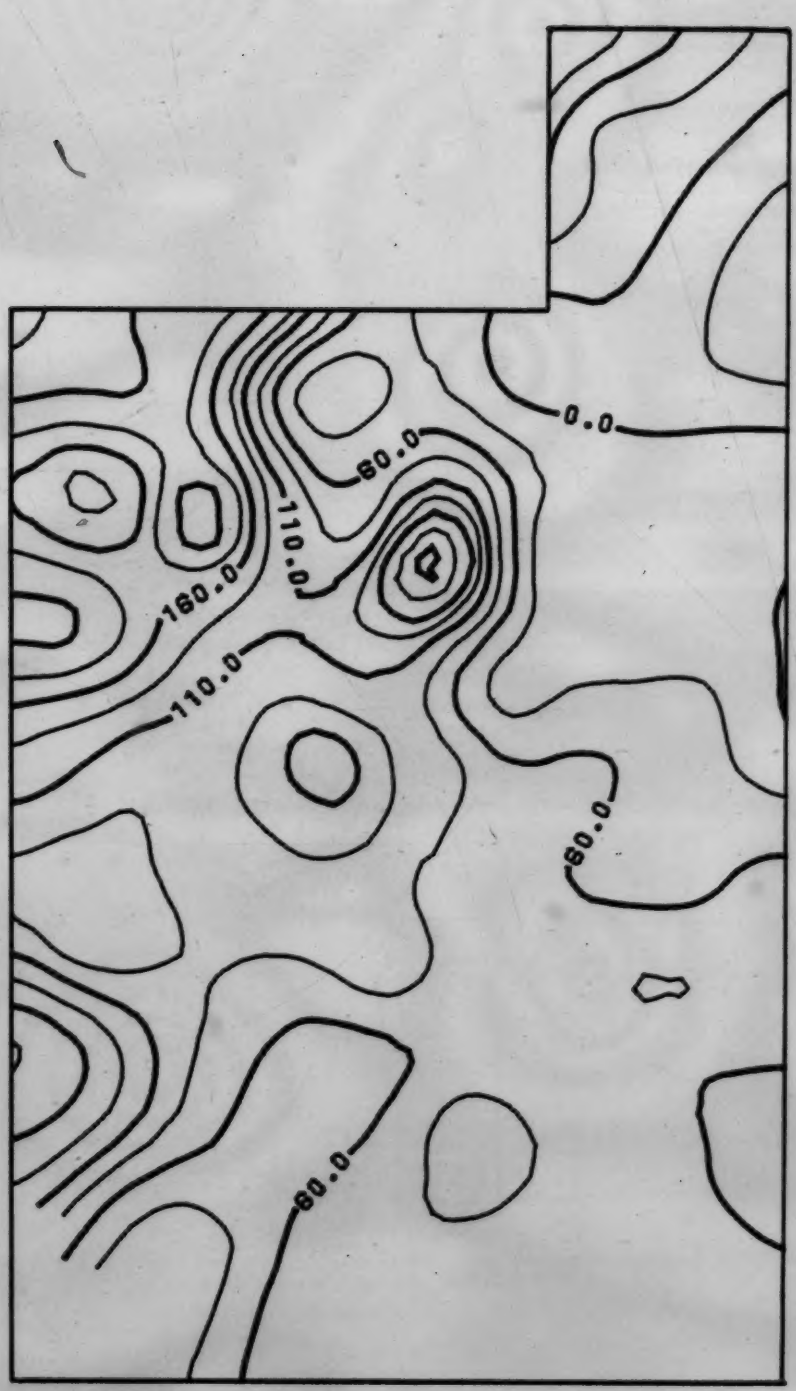

Figure 20. Contour map depicting V levels (ug gm^{-1}) in the soil parent materials of the study region.

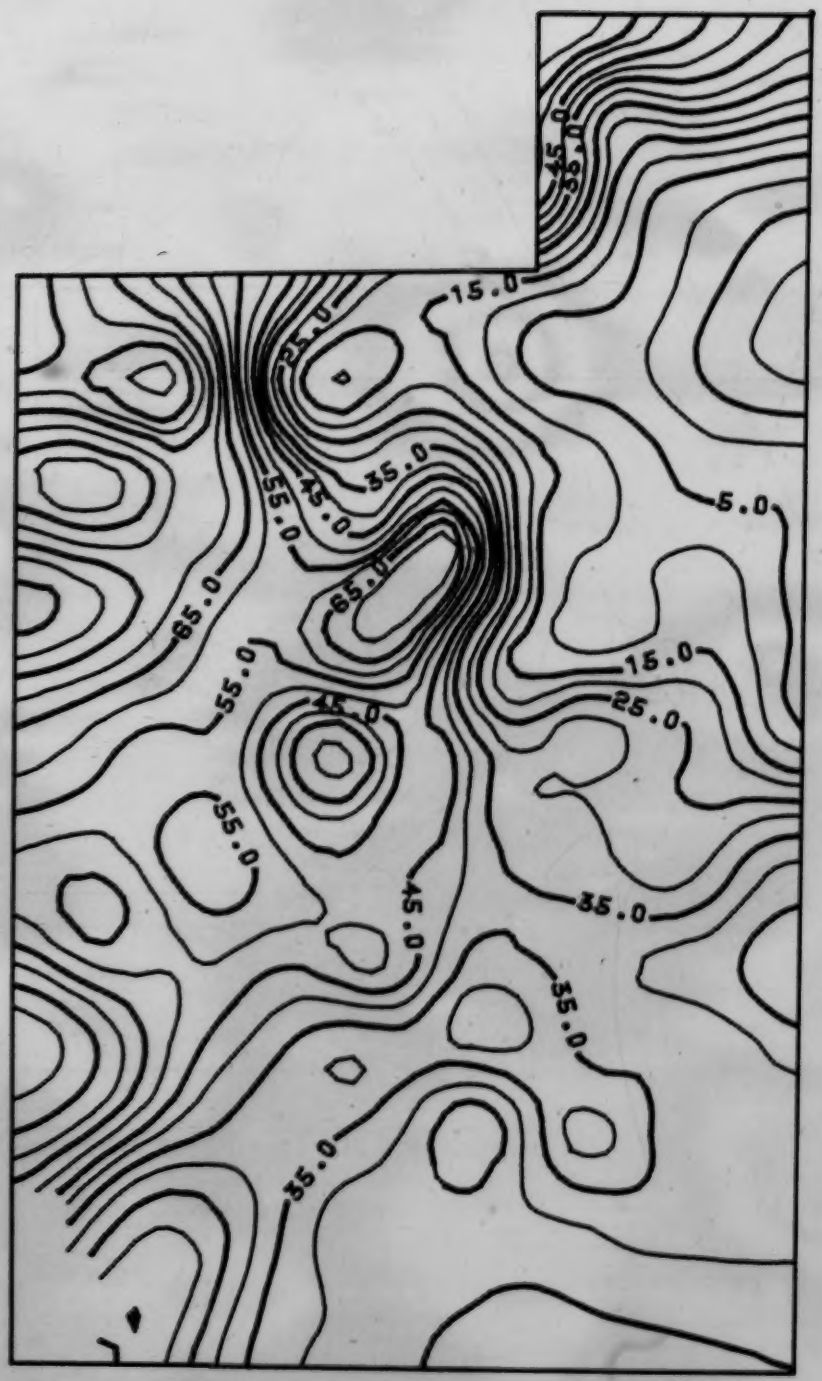

Figure 21. Contour map depicting Zn levels (ug gm^{-1}) in the soil parent materials of the study region.

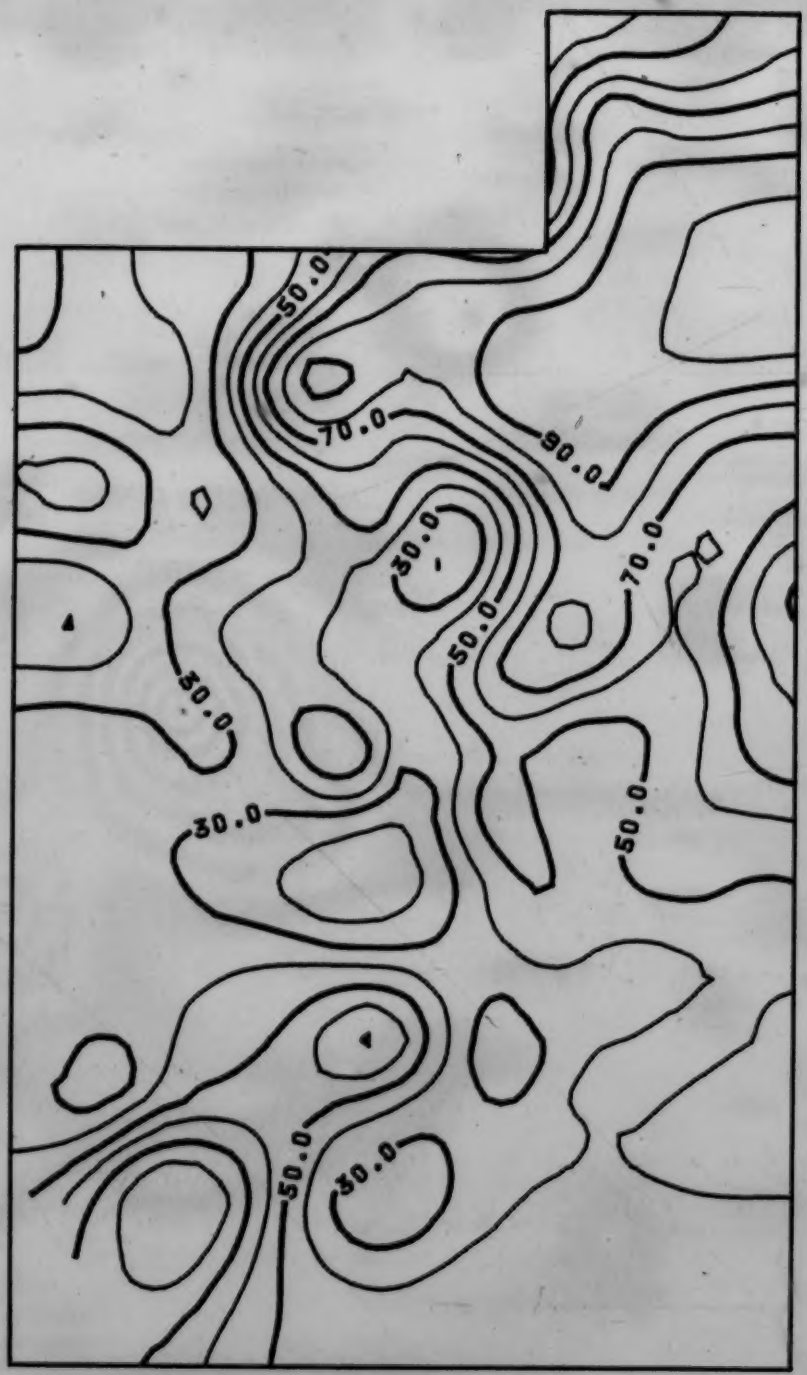

Figure 22. Contour map depicting sand levels (%) in the soil parent materials of the study region.

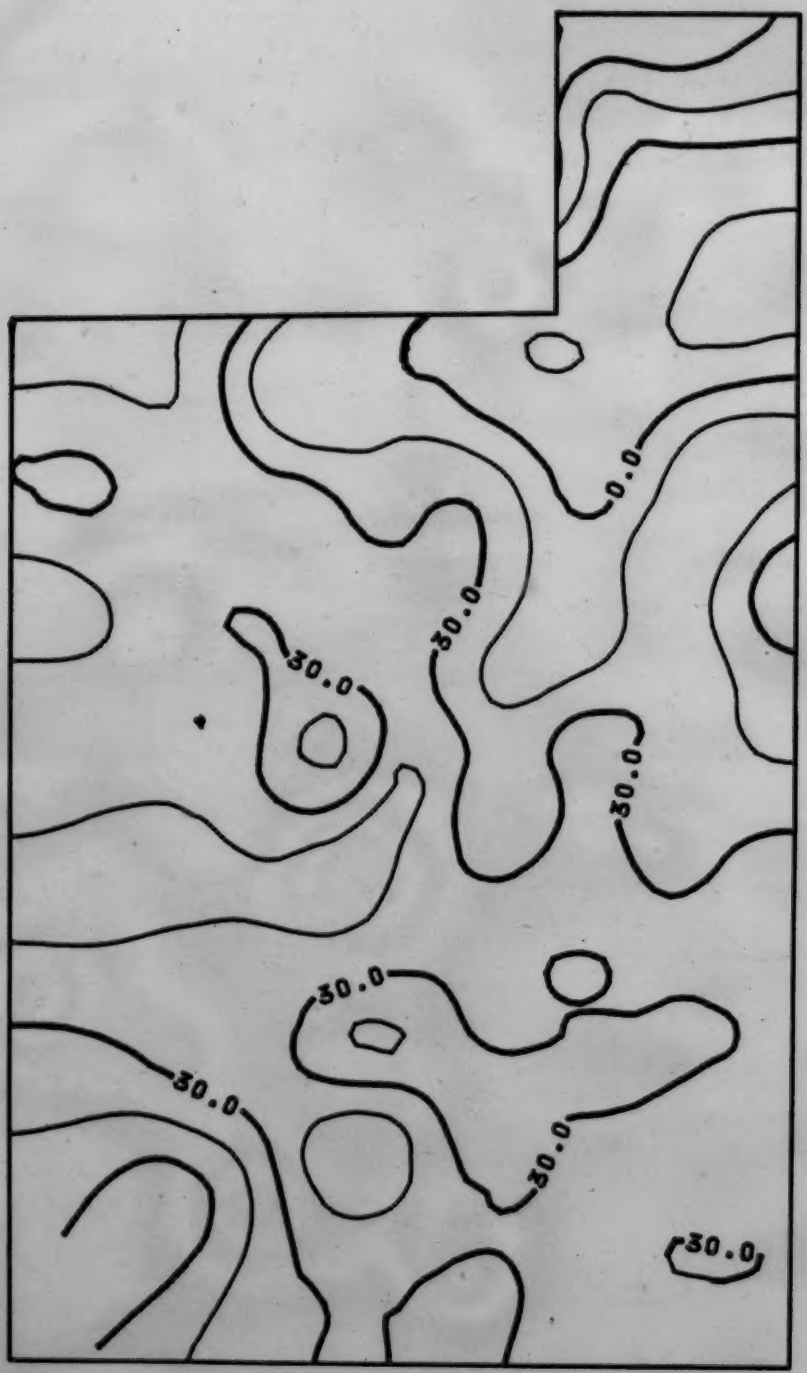

Figure 23. Contour map depicting silt levels (%) in the soil parent materials of the study region.

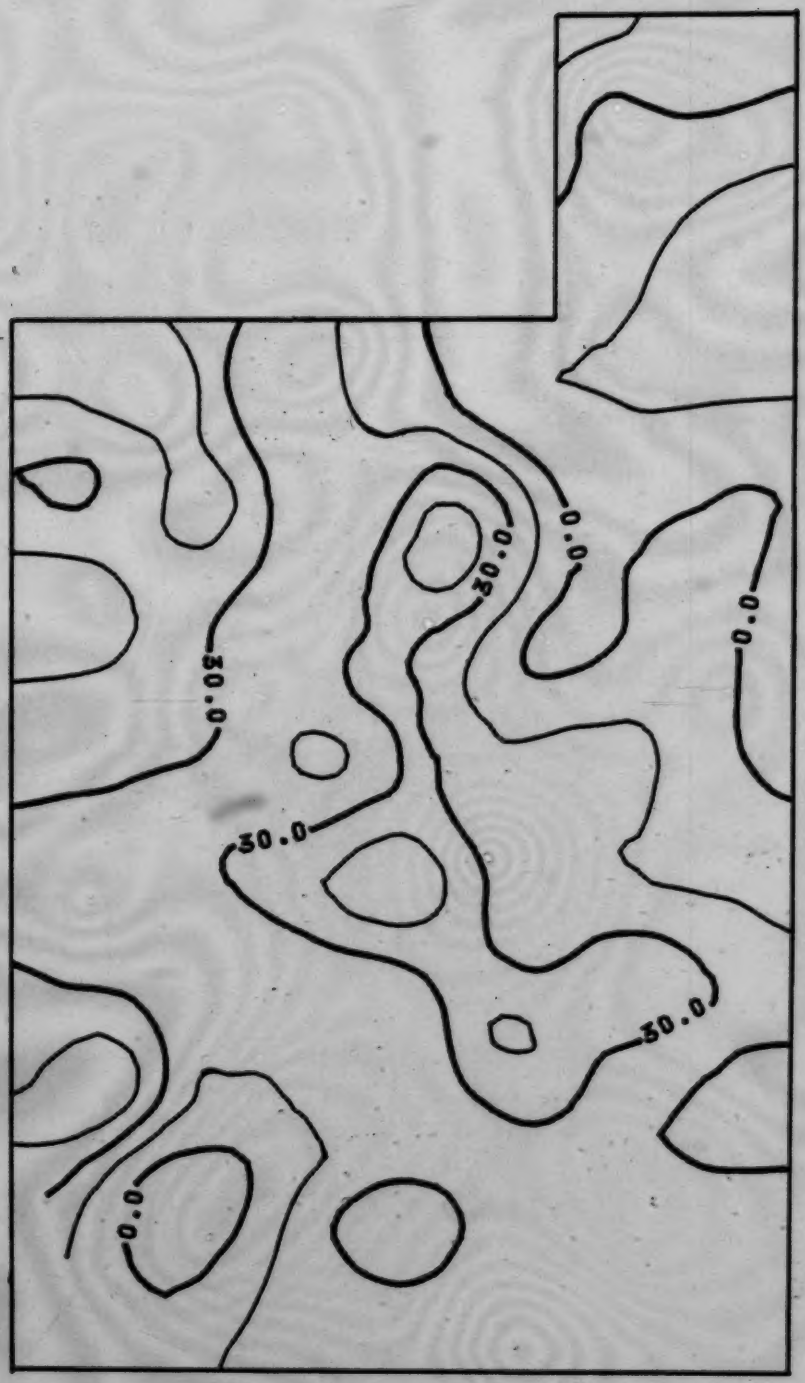

Figure 24. Contour map depicting clay levels (%) in the soil parent materials of the study region.

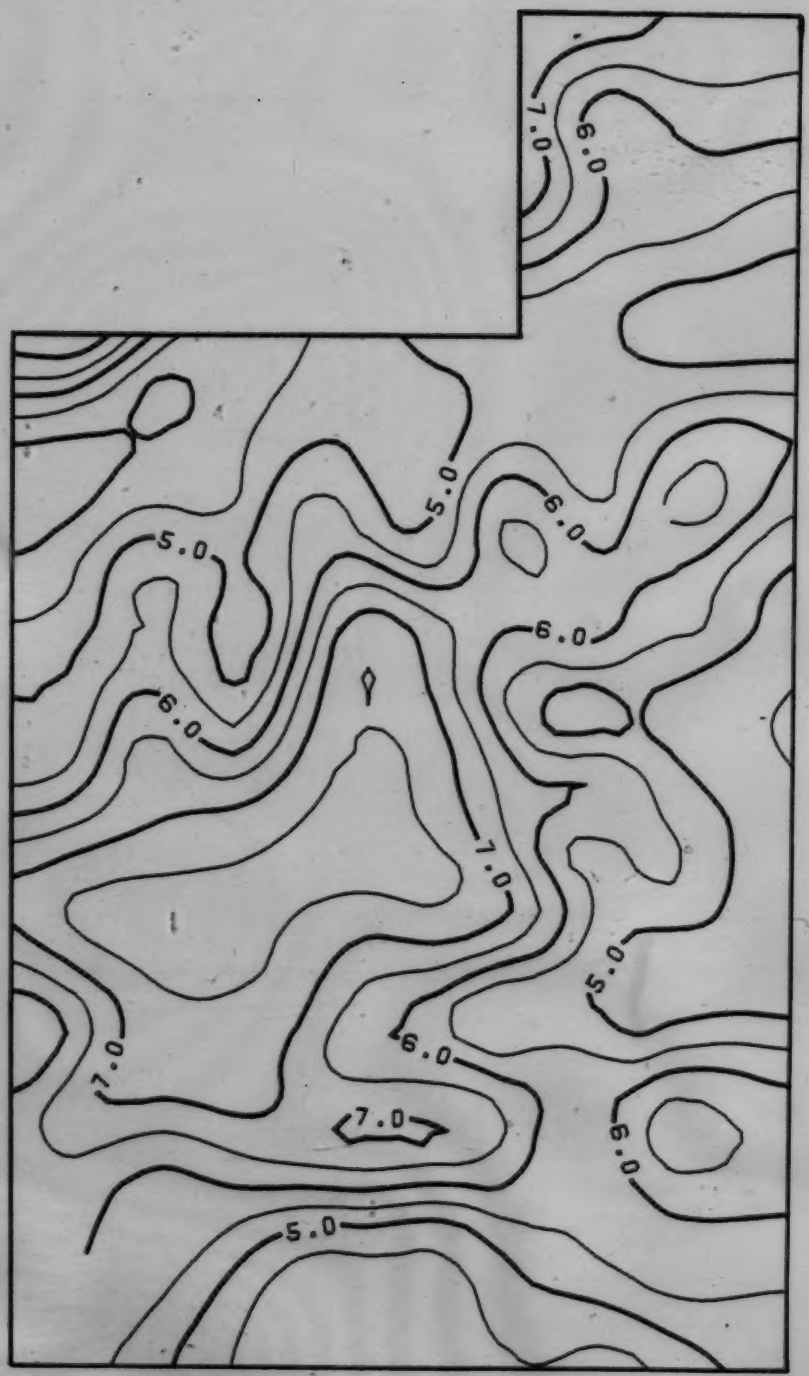

Figure 25. Contour map depicting pH variability in the soil parent materials of the study region.

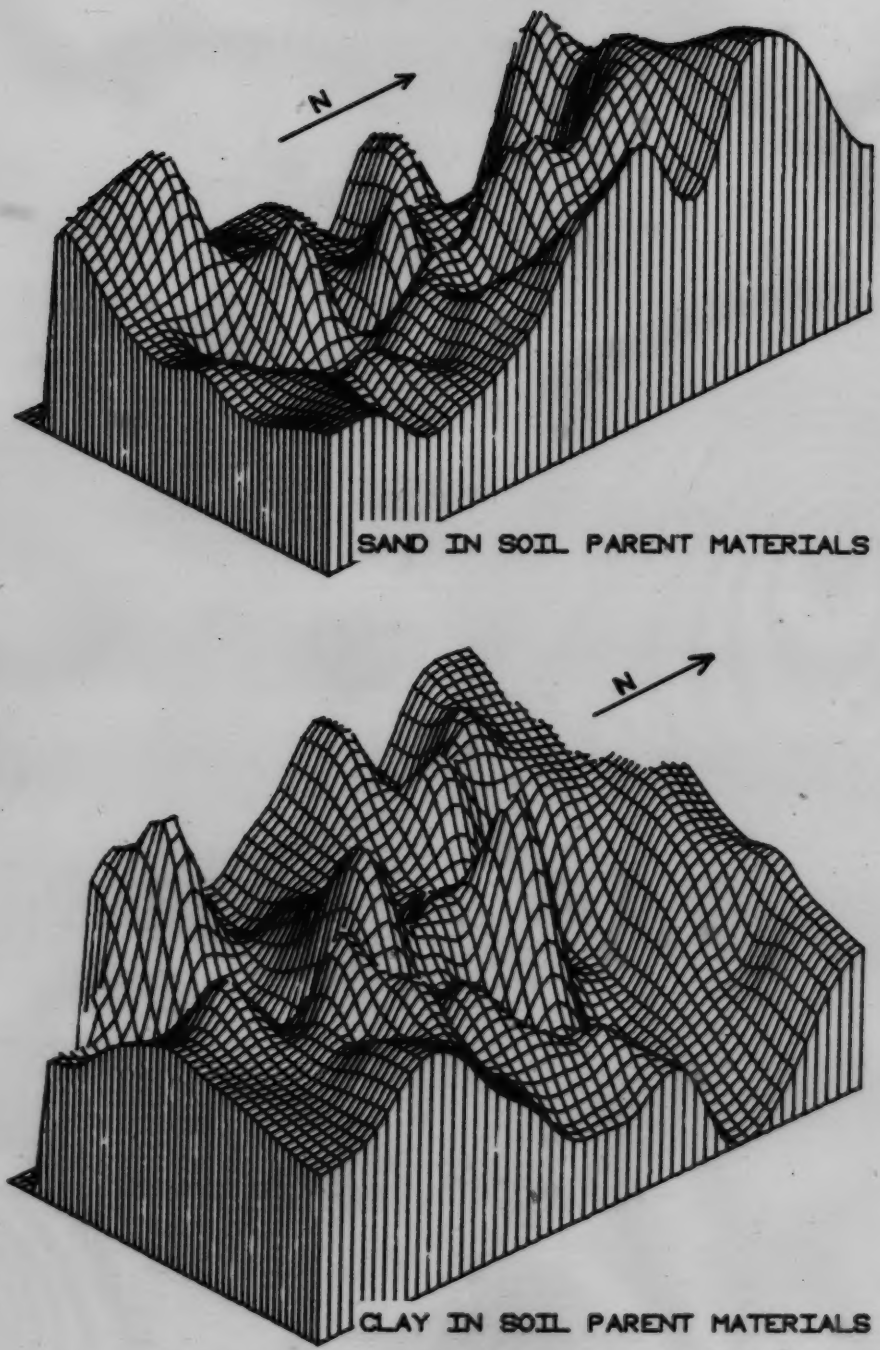

Figure 26. Block diagrams depicting the regional textural variability in the parent materials of the study area.

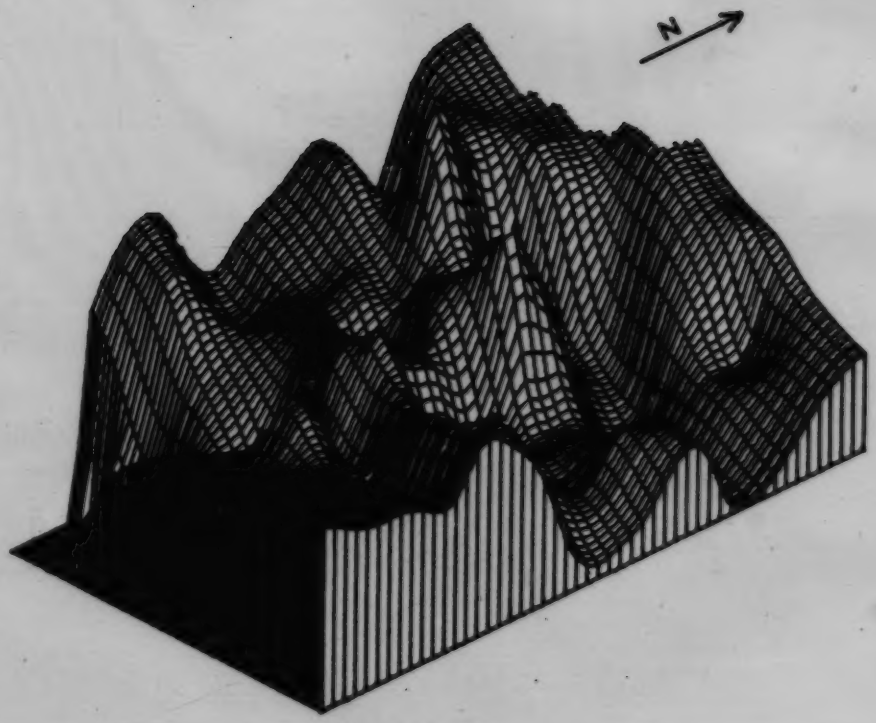

Figure 27. Block diagram depicting the regional Cu content variability in the parent materials of the study region.

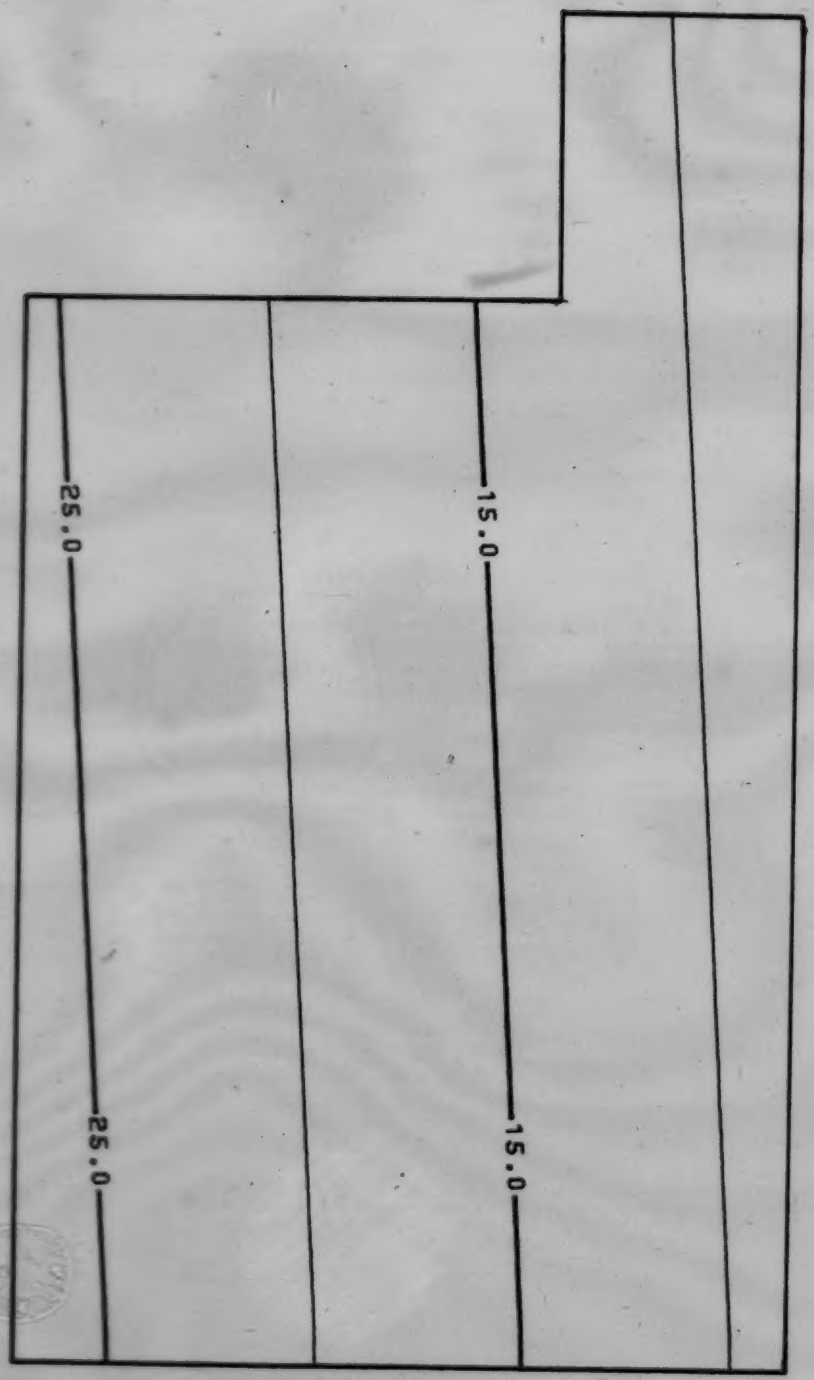

Figure 28. First order trend surface for Cu (ug gm^{-1}) in the parent materials of the study region.

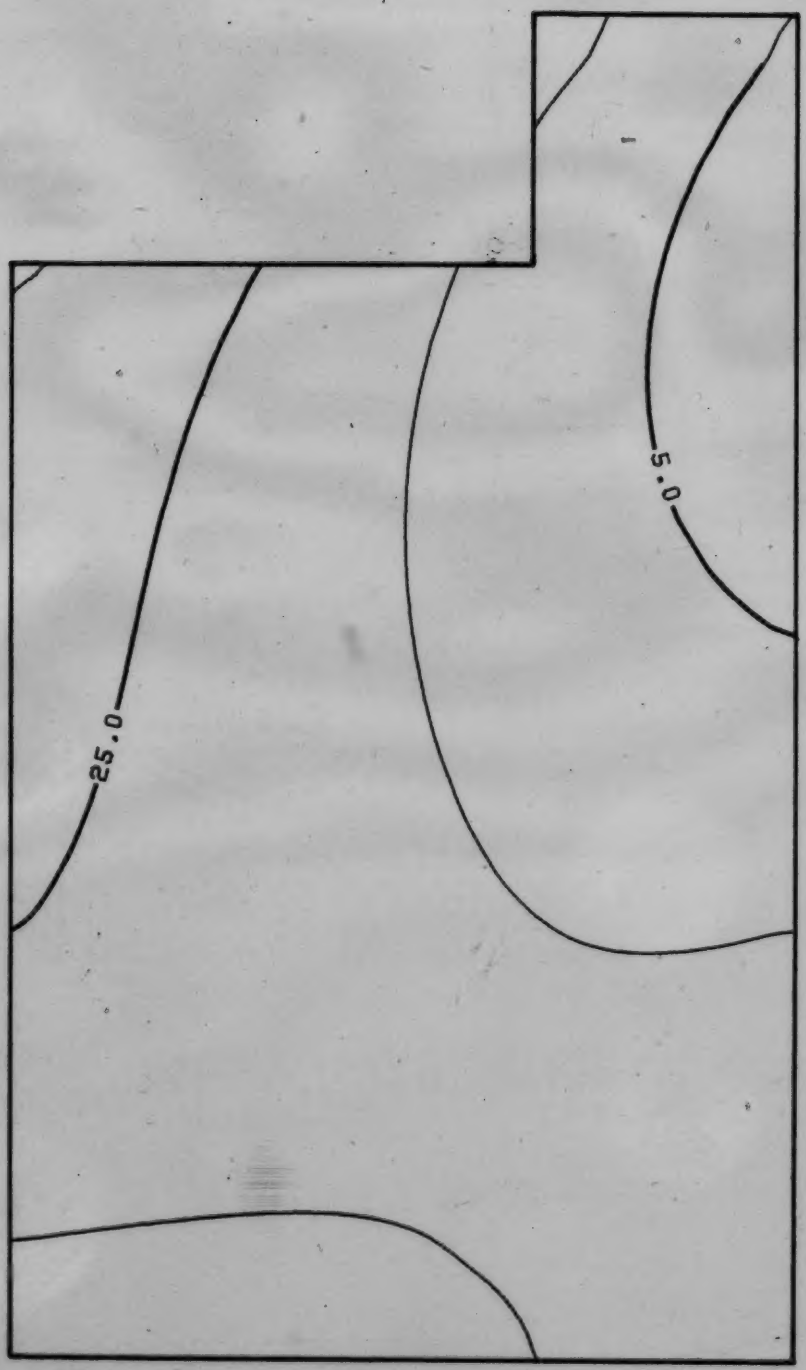

Figure 29. Cubic trend surface for Cu (ug gm^{-1}) in the parent materials of the study region.

Figure 30. First order trend surface for Cr (ug gm^{-1}) in the parent materials of the study region.

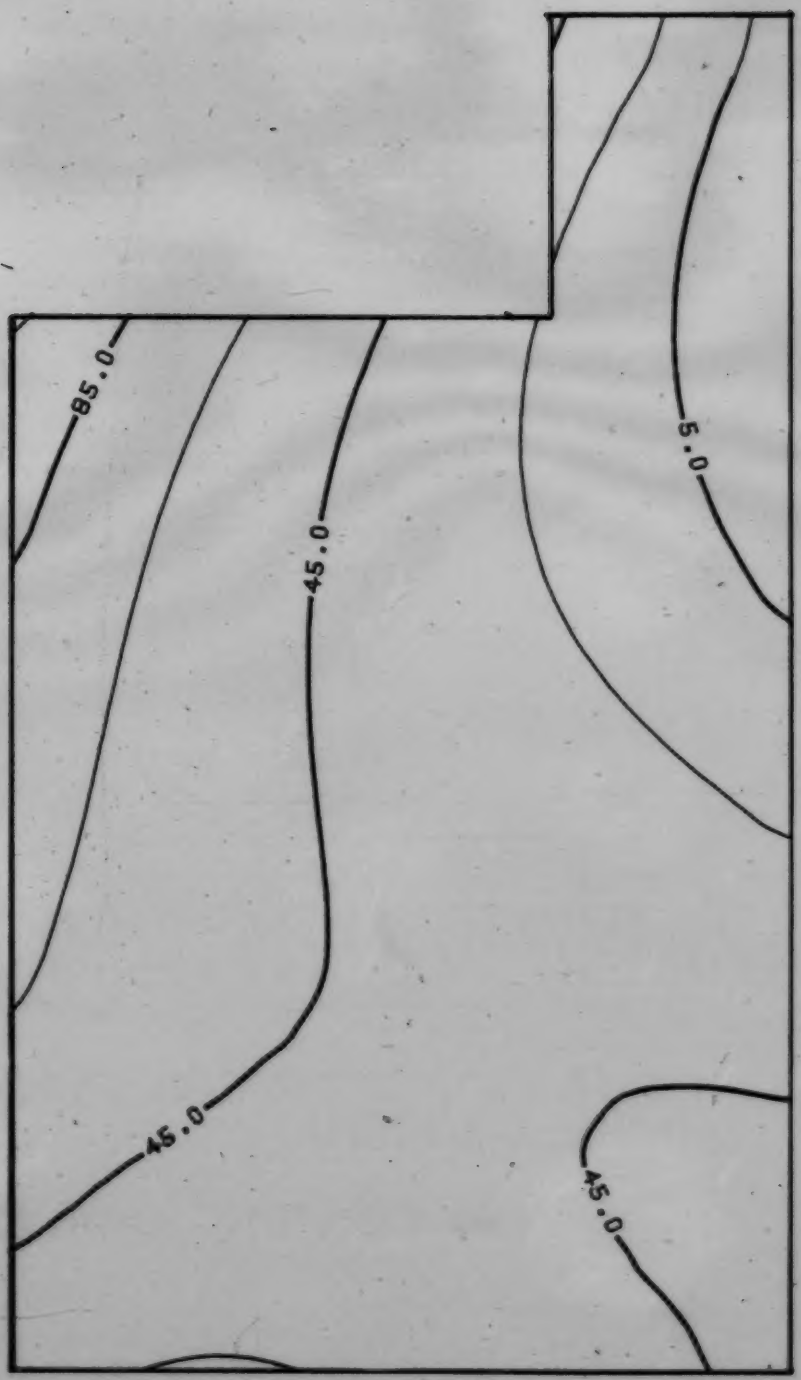

Figure 31. Cubic trend surface for Cr (ug gm^{-1}) in the parent materials of the study region.

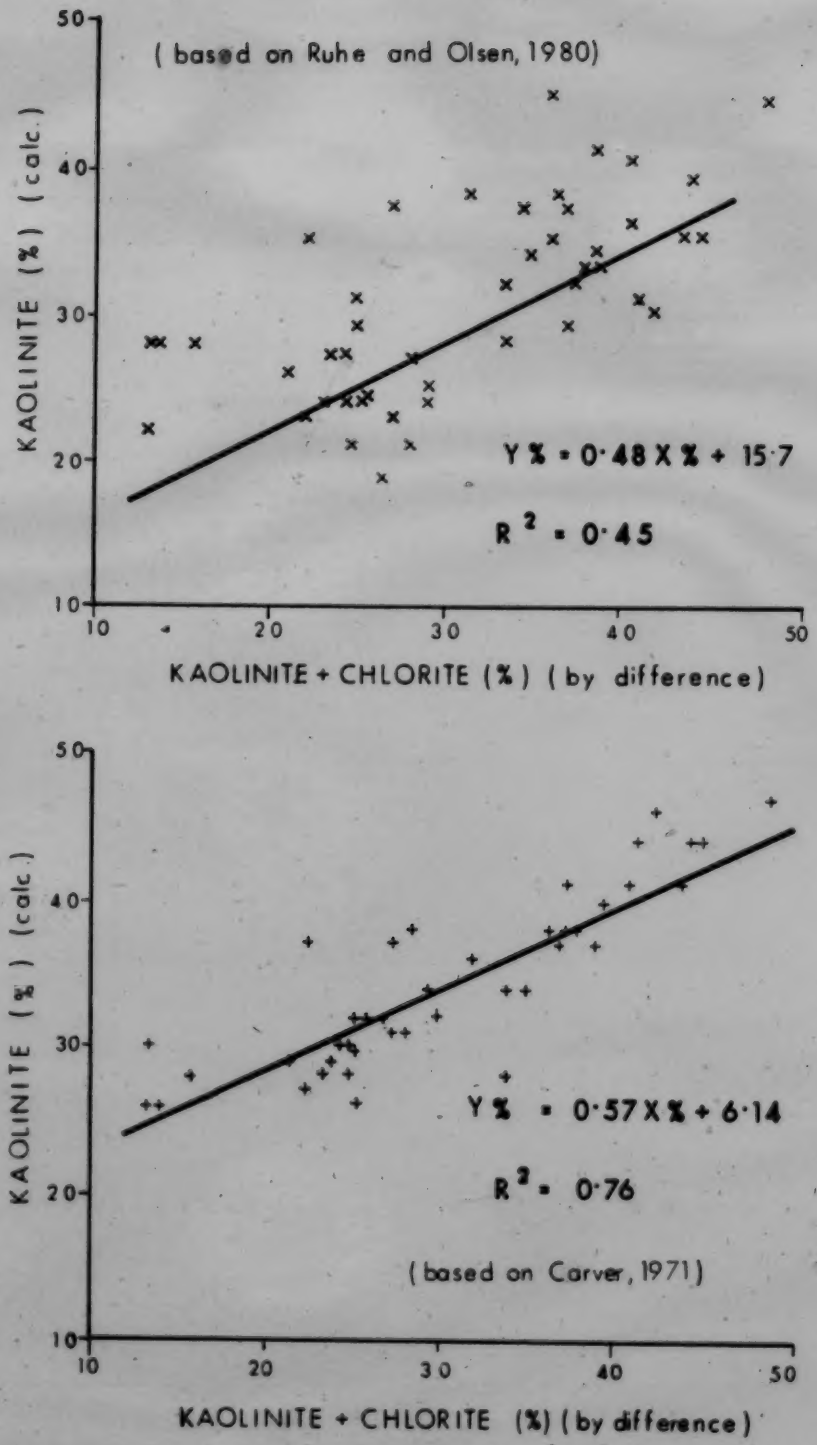
(based on Ruhe and Olsen, 1980)
KAOLINITE (%) (calc.)
KAOLINITE + CHLORITE (%) (by difference)
Y % = 0·48 X % + 15·7
R 2 = 0·45
10
20
30
40
50
KAOLINITE (%) (calc.)
KAOLINITE + CHLORITE (%) (by difference)
Y % = 0·57 X % + 6·14
R 2 = 0·76
(based on Carver, 1971)

Figure 32. Comparison of estimates of kaolinite content in the clay fraction of the parent materials of the study region.

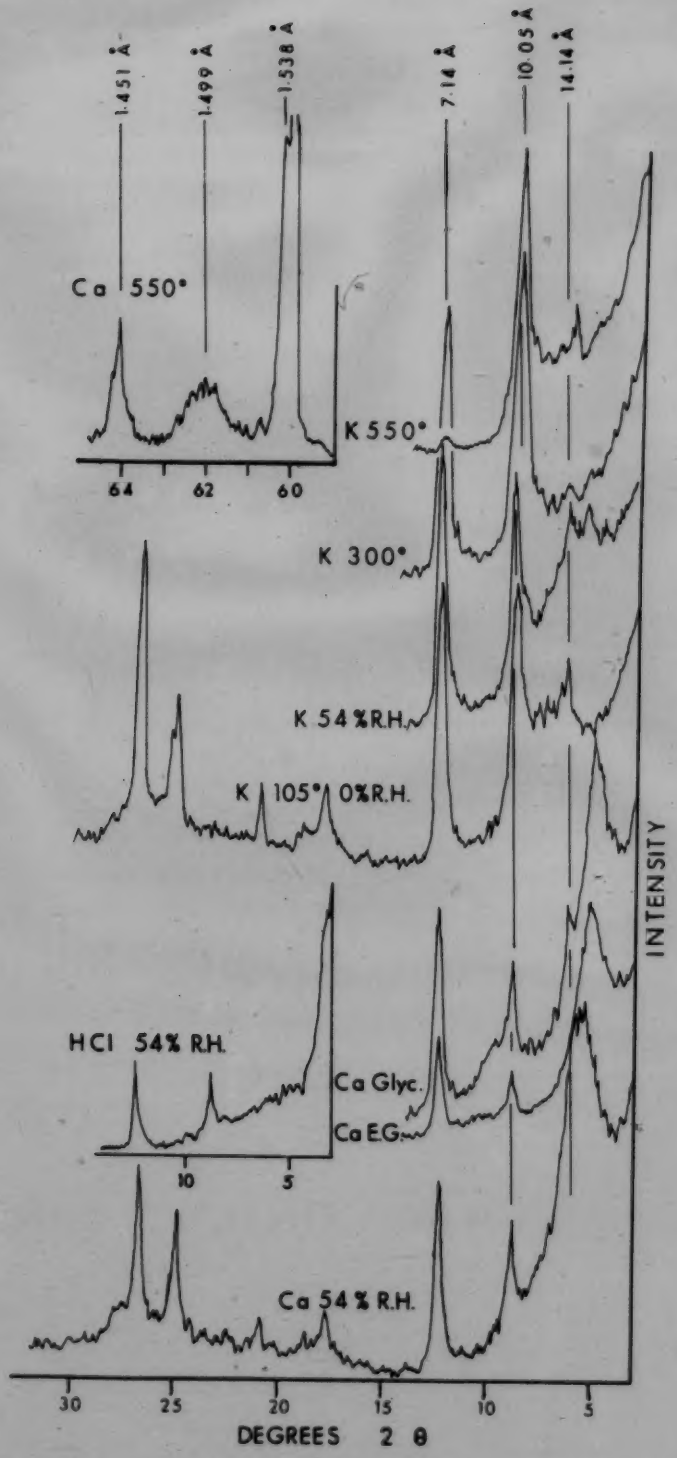

Figure 33. X-ray diffractograms representative of the bulk clay separates of the Dover Soil Unit.

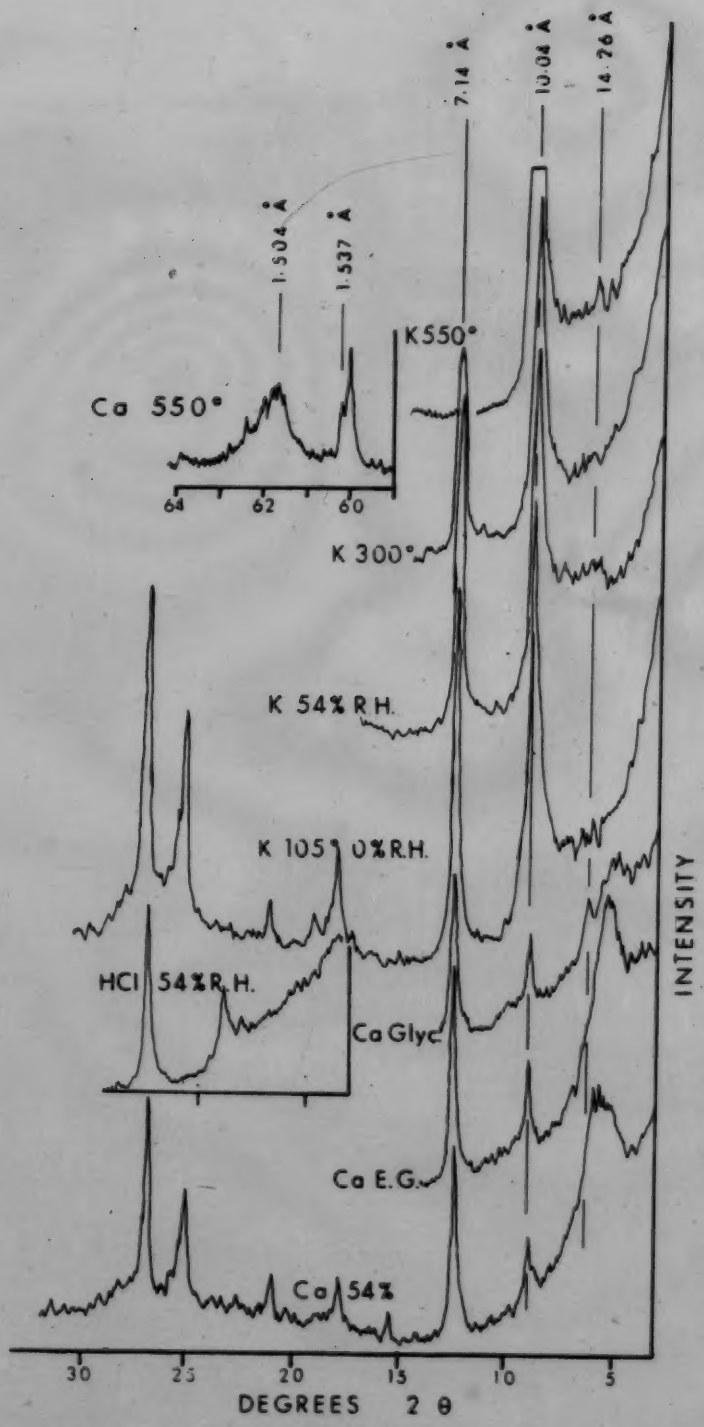

Figure 34. X-ray diffractograms representative of the bulk clay separates of the Kinosis Soil Unit.

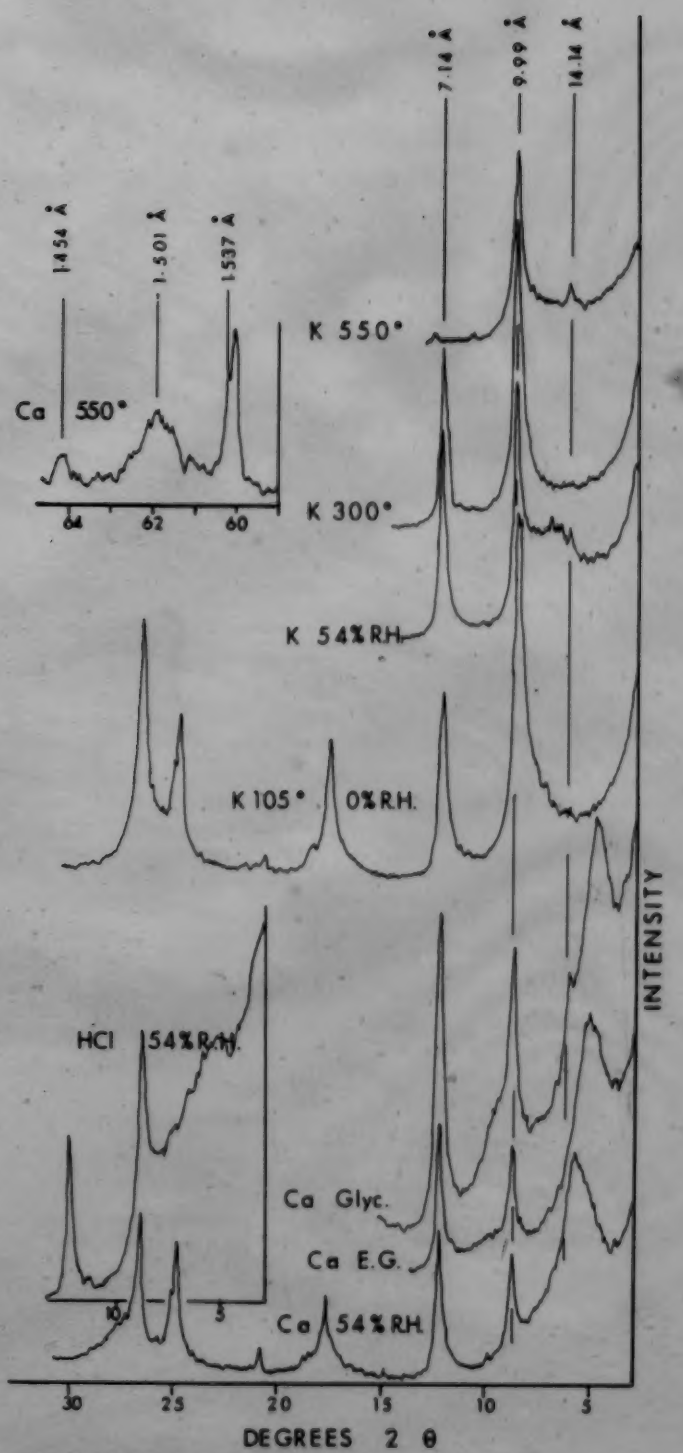

Figure 35. X-ray diffractograms representative of the bulk clay separates of the Horse River Soil Unit.

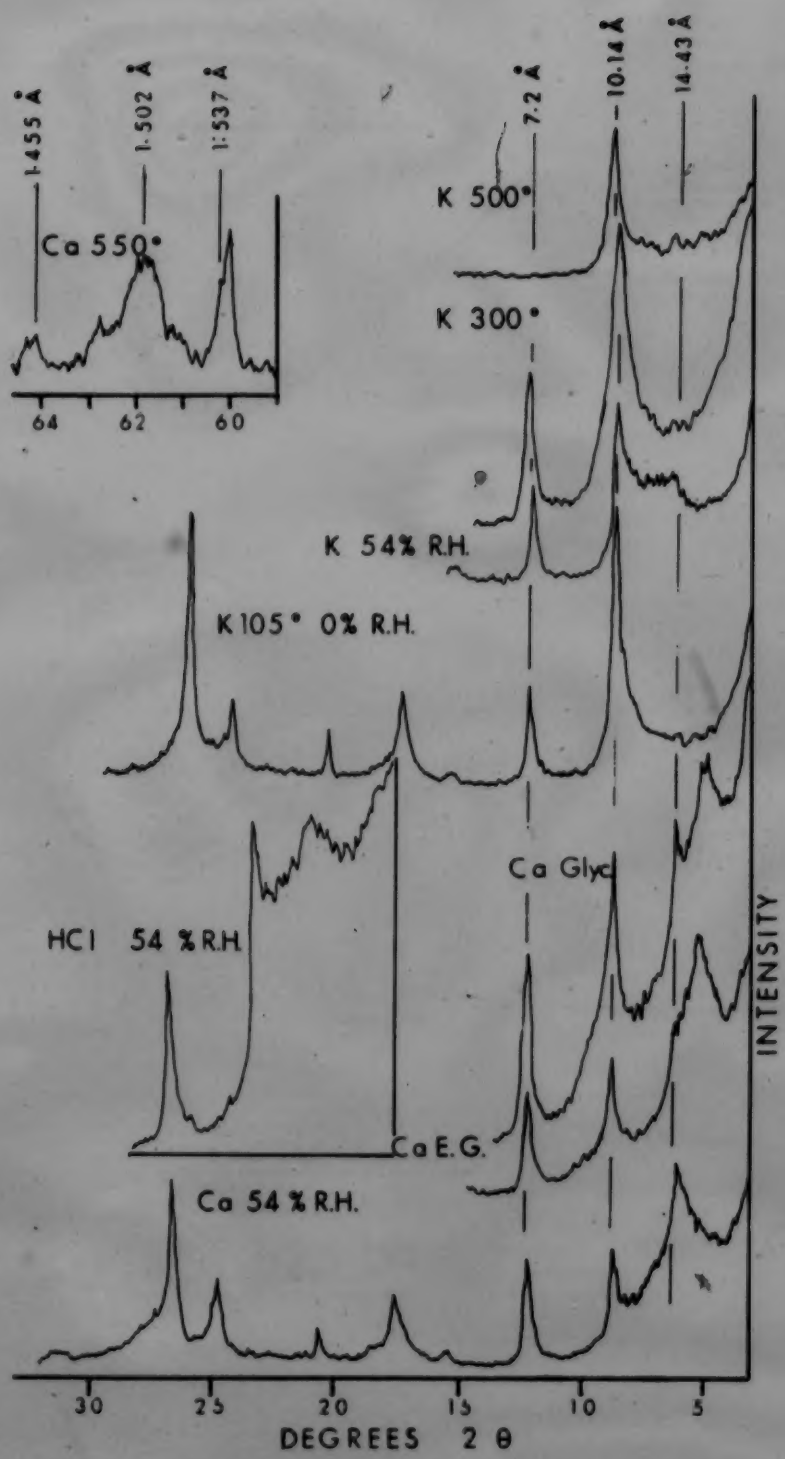

Figure 36. X-ray diffractograms representative of the bulk clay separates of the Legend Soil Unit.

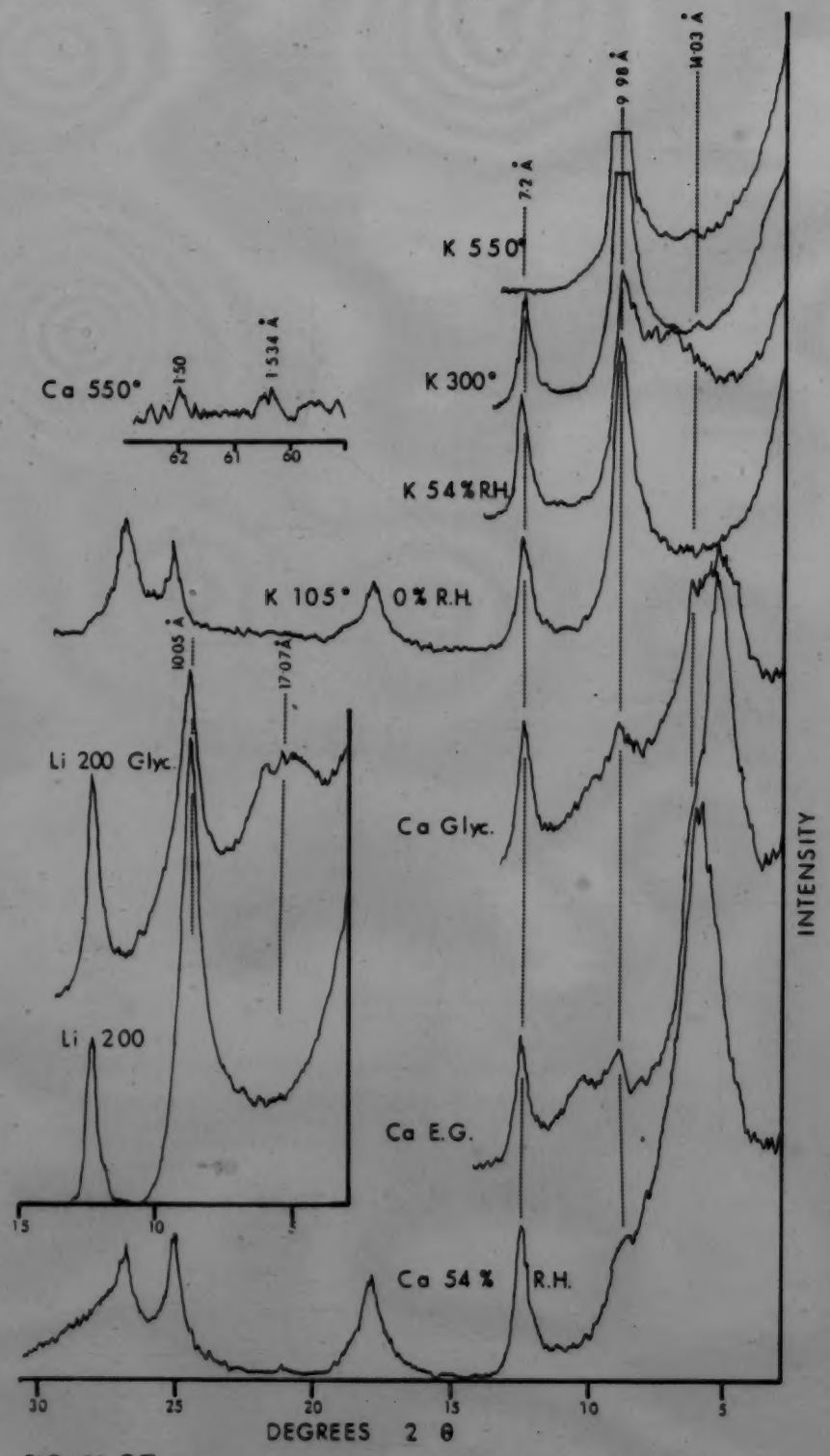

FIGURE: 37: X-RAY DIFFRACTOGRAMS OF FINE CLAY SEPARATES REPRESENTATIVE OF THE KINOSIS SOIL UNIT.

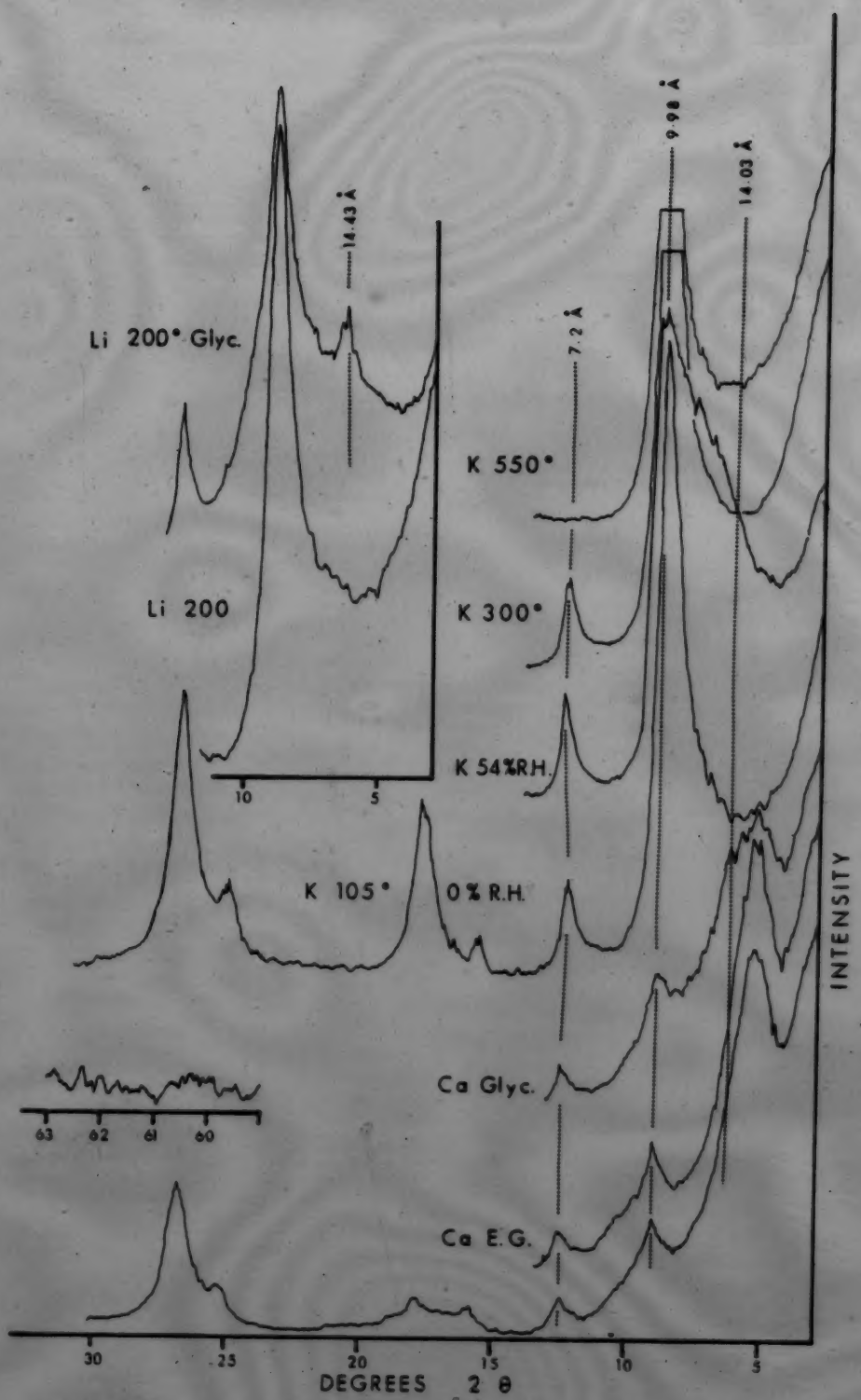

FIGURE:38: X-RAY DIFFRACTOGRAMS OF FINE CLAY SEPARATES REPRESENTATIVE OF THE LEGEND SOIL UNIT

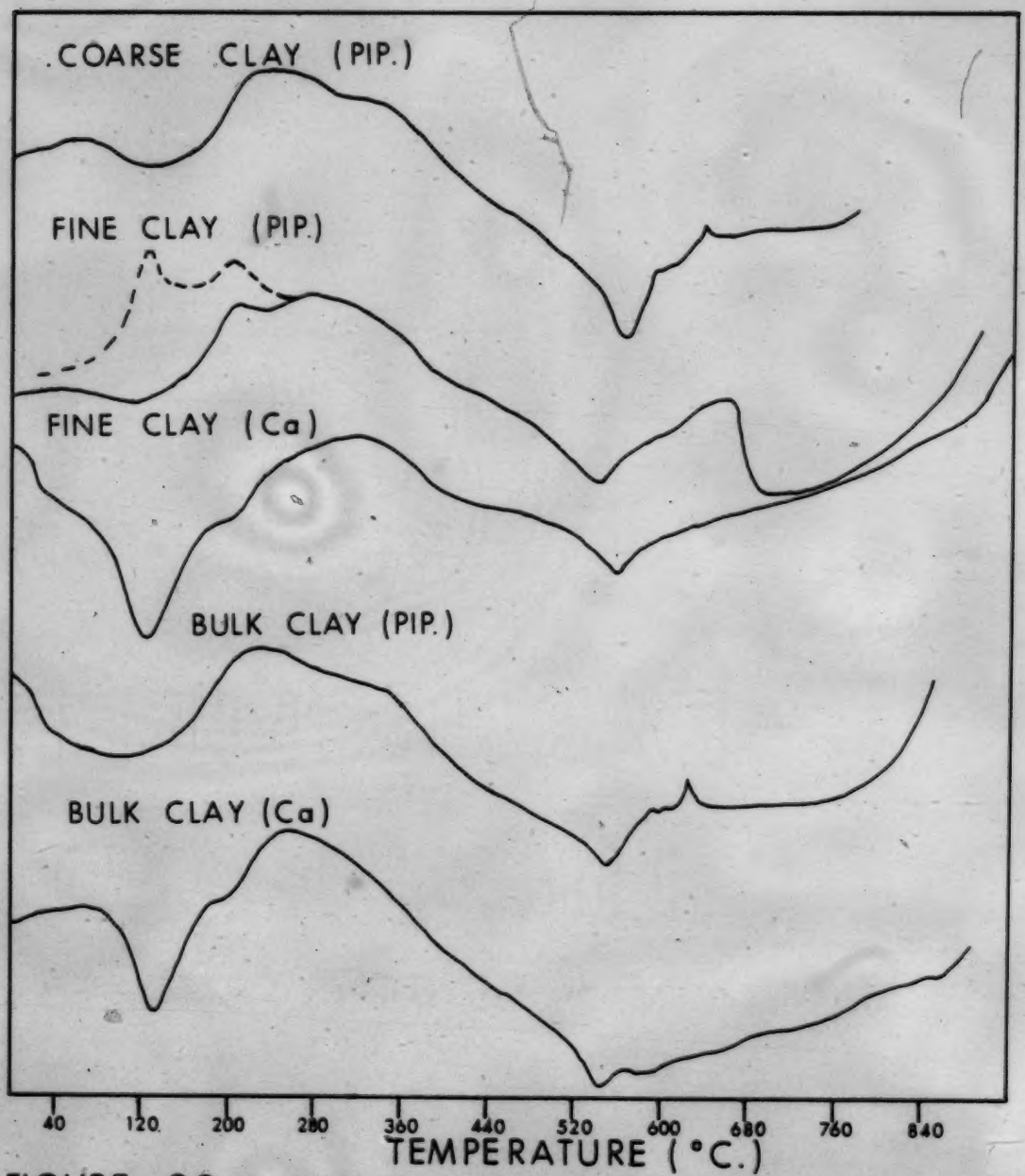

FIGURE: 39: DIFFERENTIAL THERMOGRAPHS OF CLAY SEPARATES FROM THE KINOSIS SOIL UNIT.

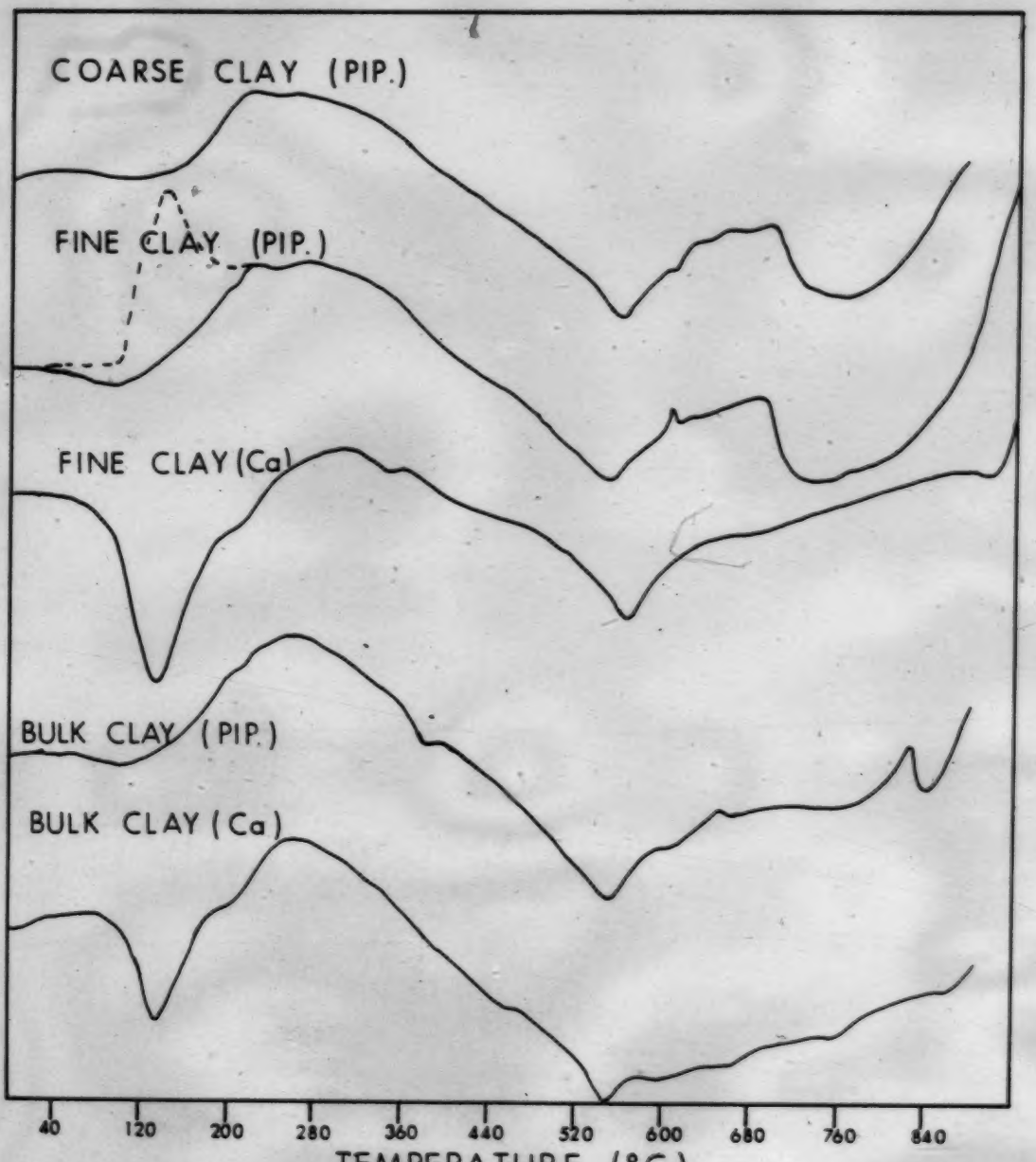

FIGURE: 40 : DIFFERENTIAL THERMOGRAPHS OF CLAY SEPARATES FROM THE LEGEND SOIL UNIT.

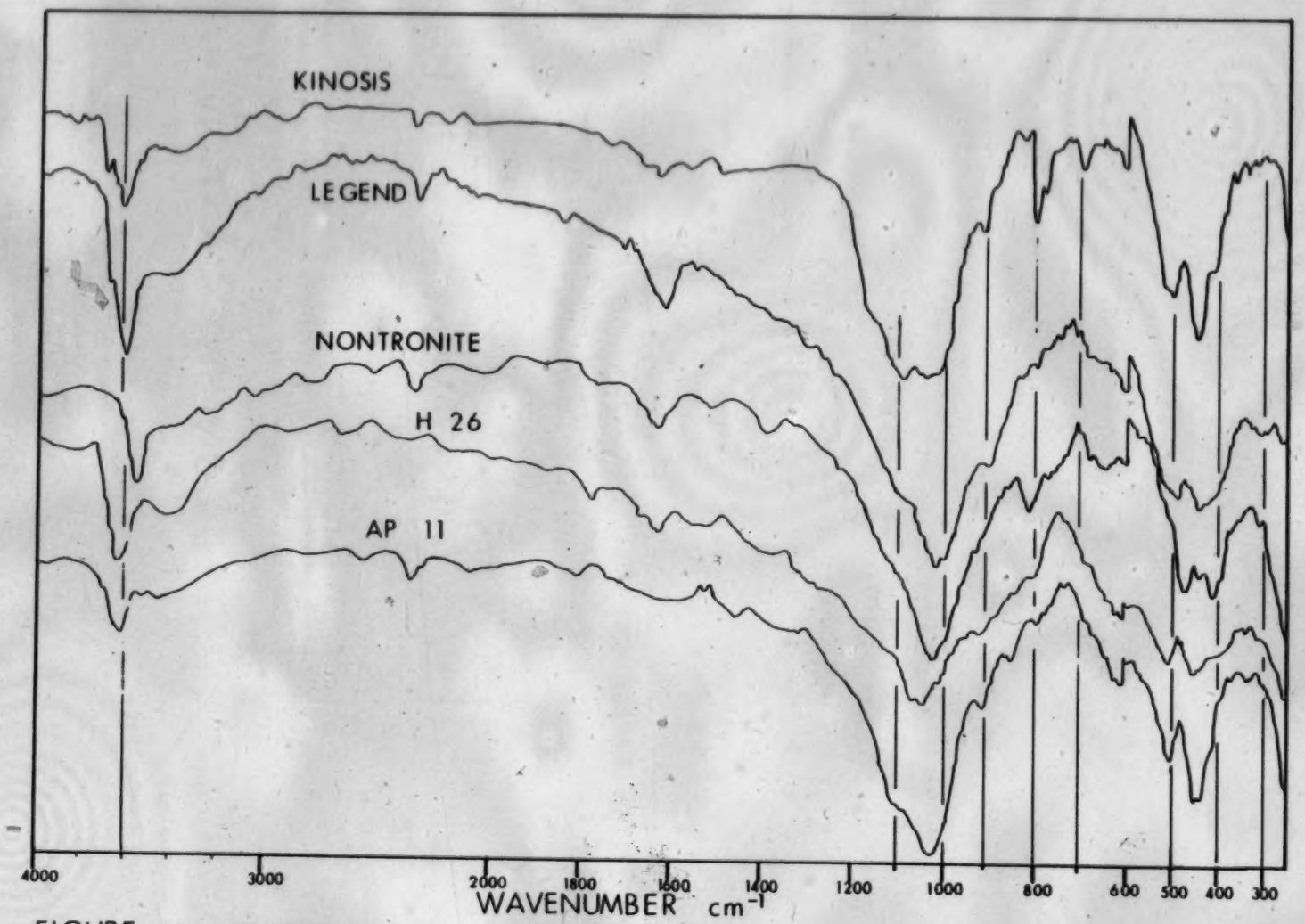

FIGURE: 41 : INRARED SPECTRA OF FINE CLAY SEPARATES FROM THE KINOSIS AND LEGEND SOIL UNITS, AND OF A.P.I. REFERENCE MINERALS.

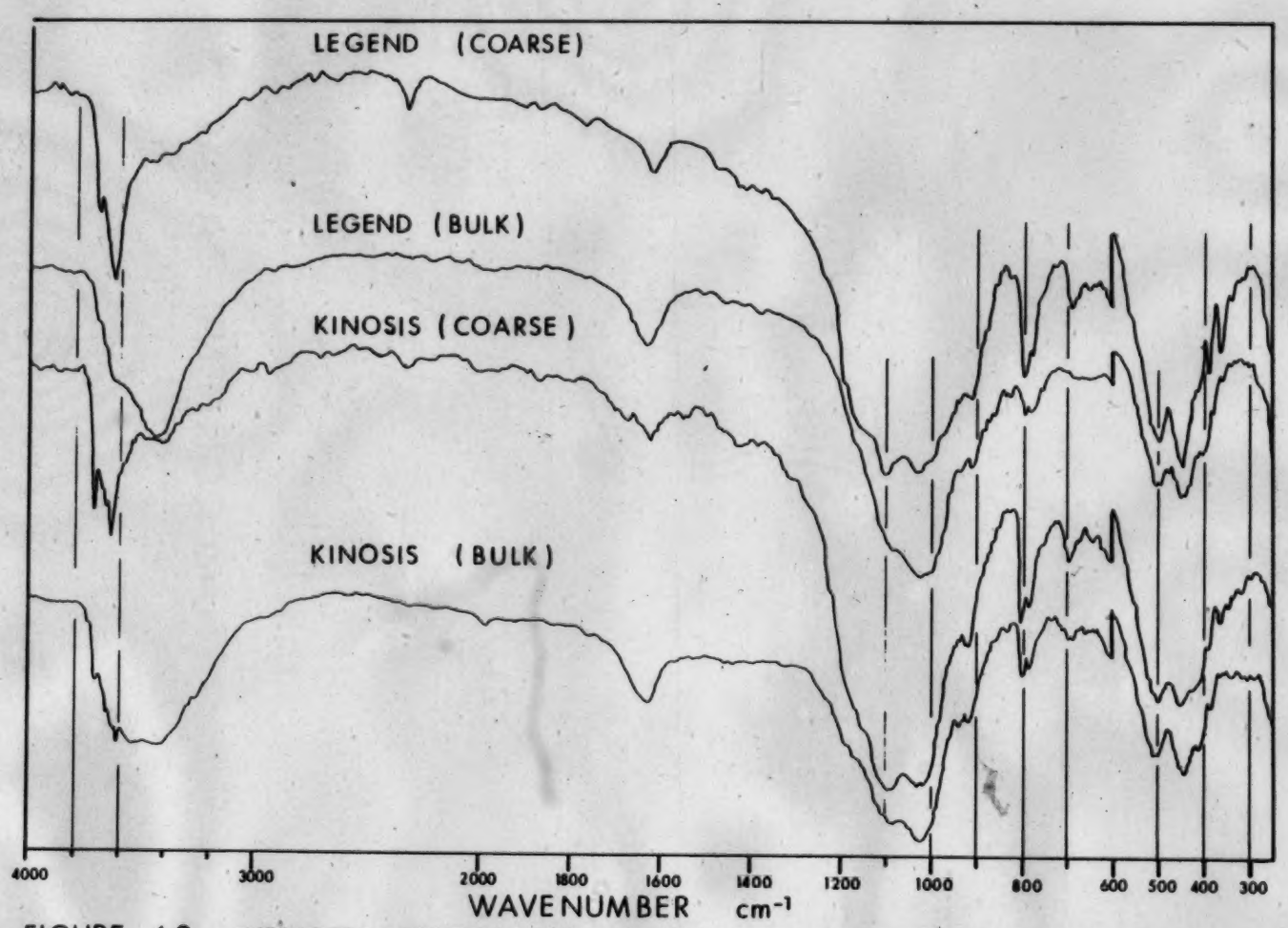

FIGURE: 42 : INFRARED SPECTRA OF COARSE AND BULK CLAY SEPARATES FROM THE LEGEND AND KINOSIS SOIL UNITS.

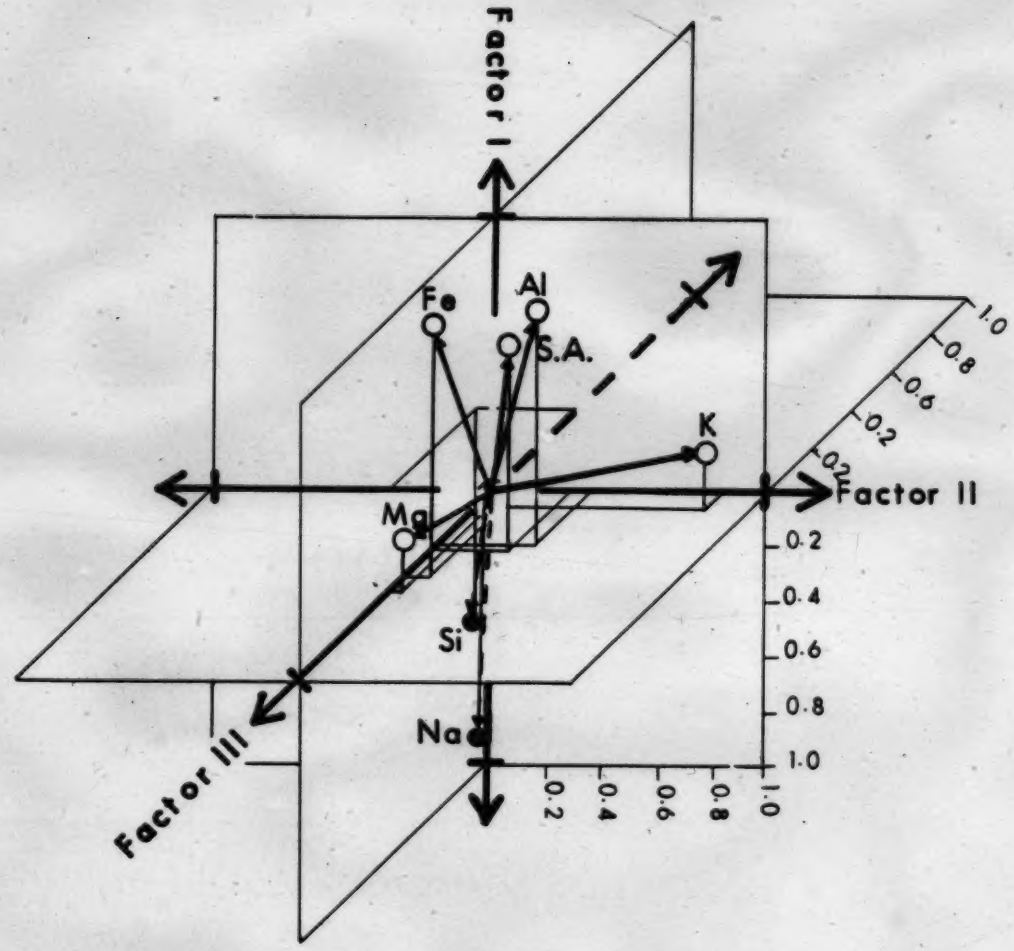

FIGURE: 43 : TRIAXIAL PROJECTIONS OF FACTOR LOADINGS BY CHEMICAL VARIABLES FROM THE VARIMAX ROTATED FACTOR MATRIX. (MACROELEMENTS)

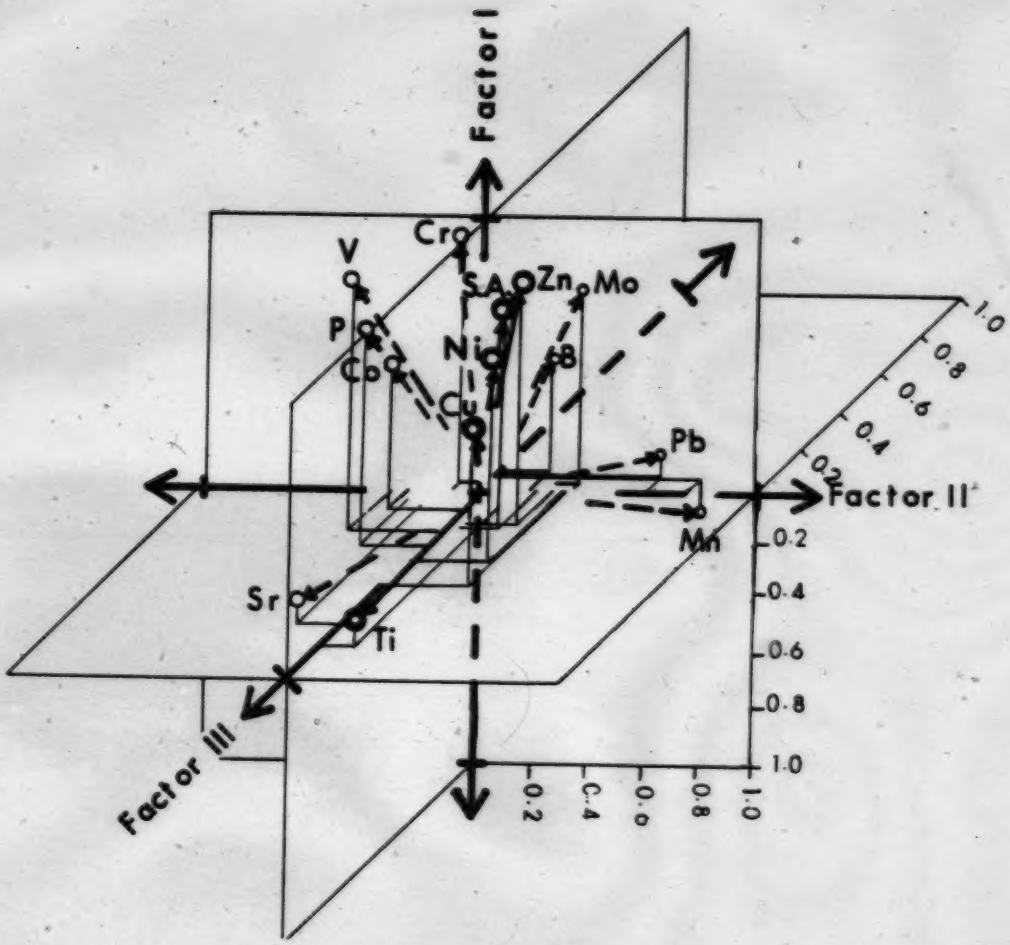

FIGURE: 44: TRIAXIAL PROJECTIONS OF FACTOR LOADINGS BY CHEMICAL VARIABLES FROM THE VARIMAX ROTATED FACTOR MATRIX. (MINOR ELEMENTS).

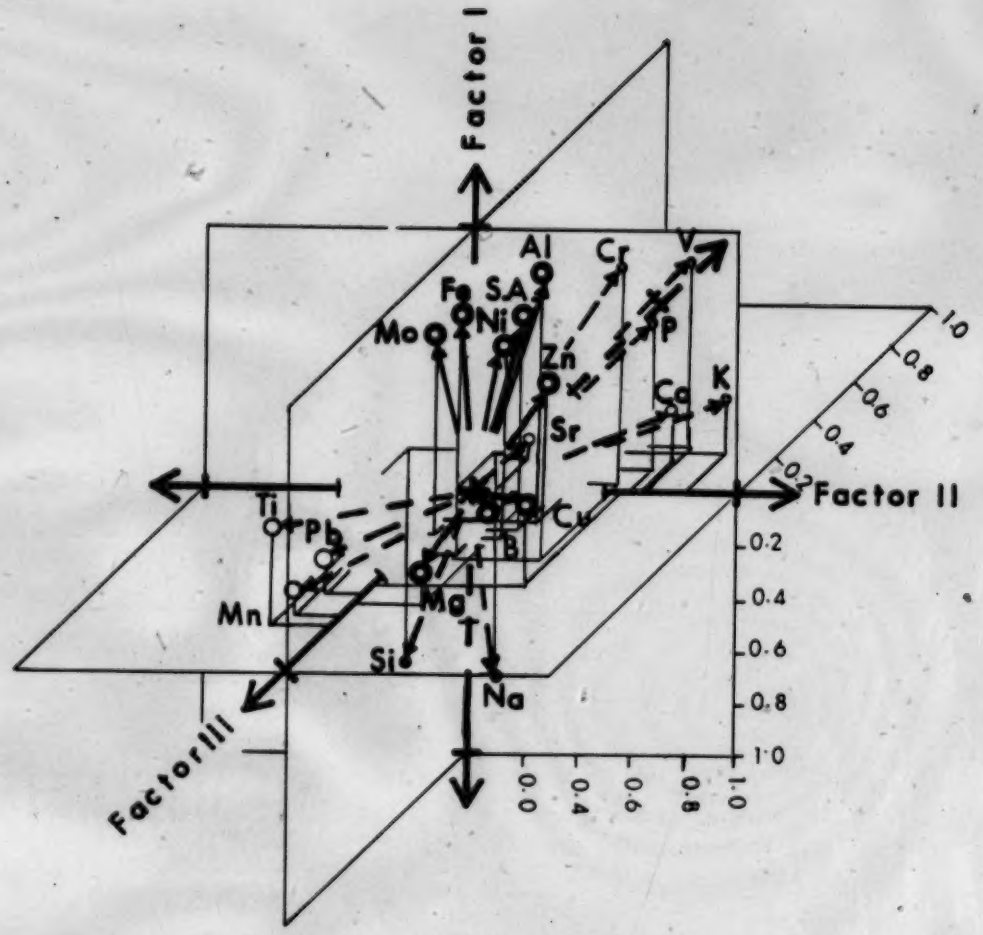

FIGURE: 45 : TRIAXIAL PROJECTIONS OF FACTOR LOADINGS BY CHEMICAL VARIABLES FROM THE VARIMAX ROTATED FACTOR MATRIX. (TOTAL ELEMENTAL COMPOSITION).

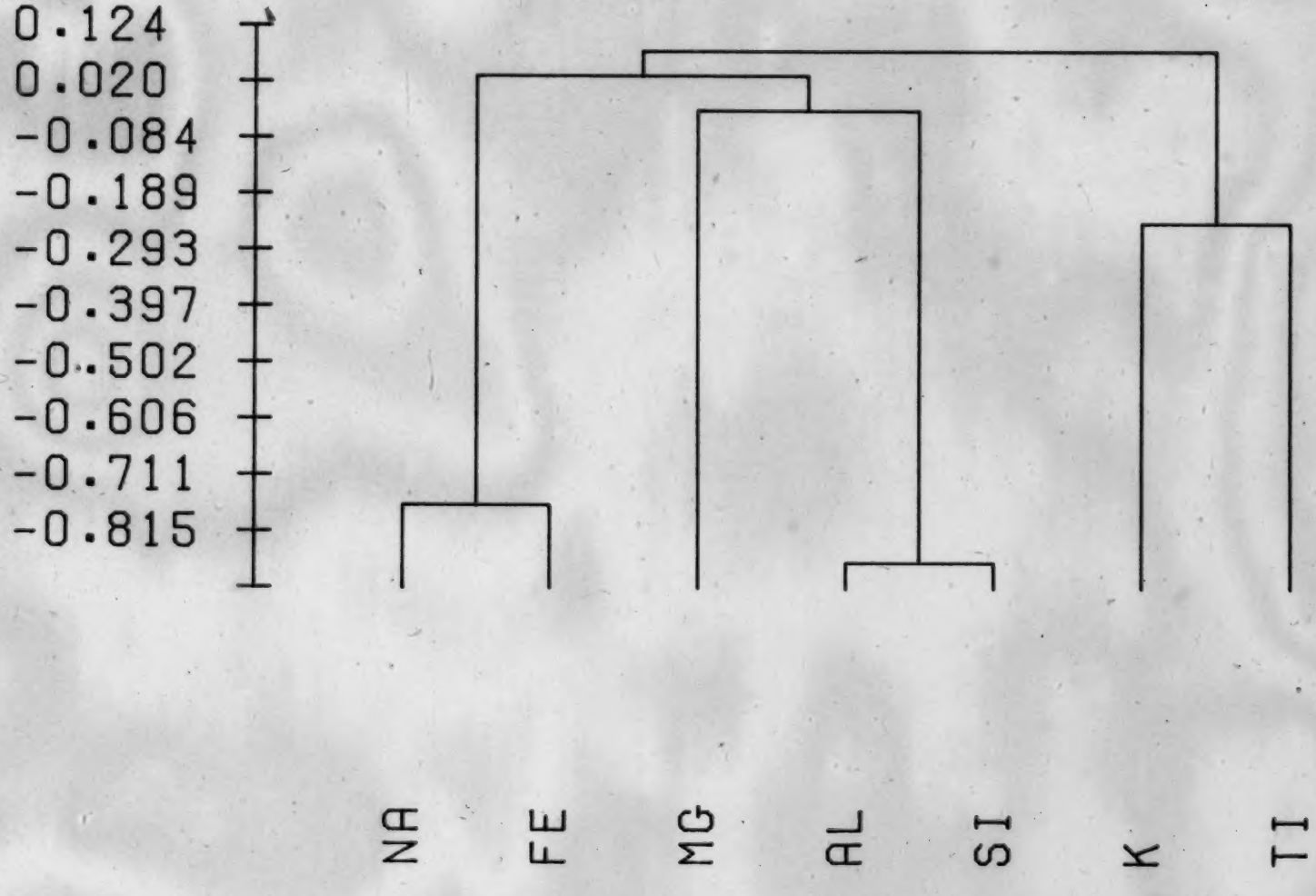

Figure 46. Dendrogram displaying the relationship between the major elements in the clay separates from the study region).

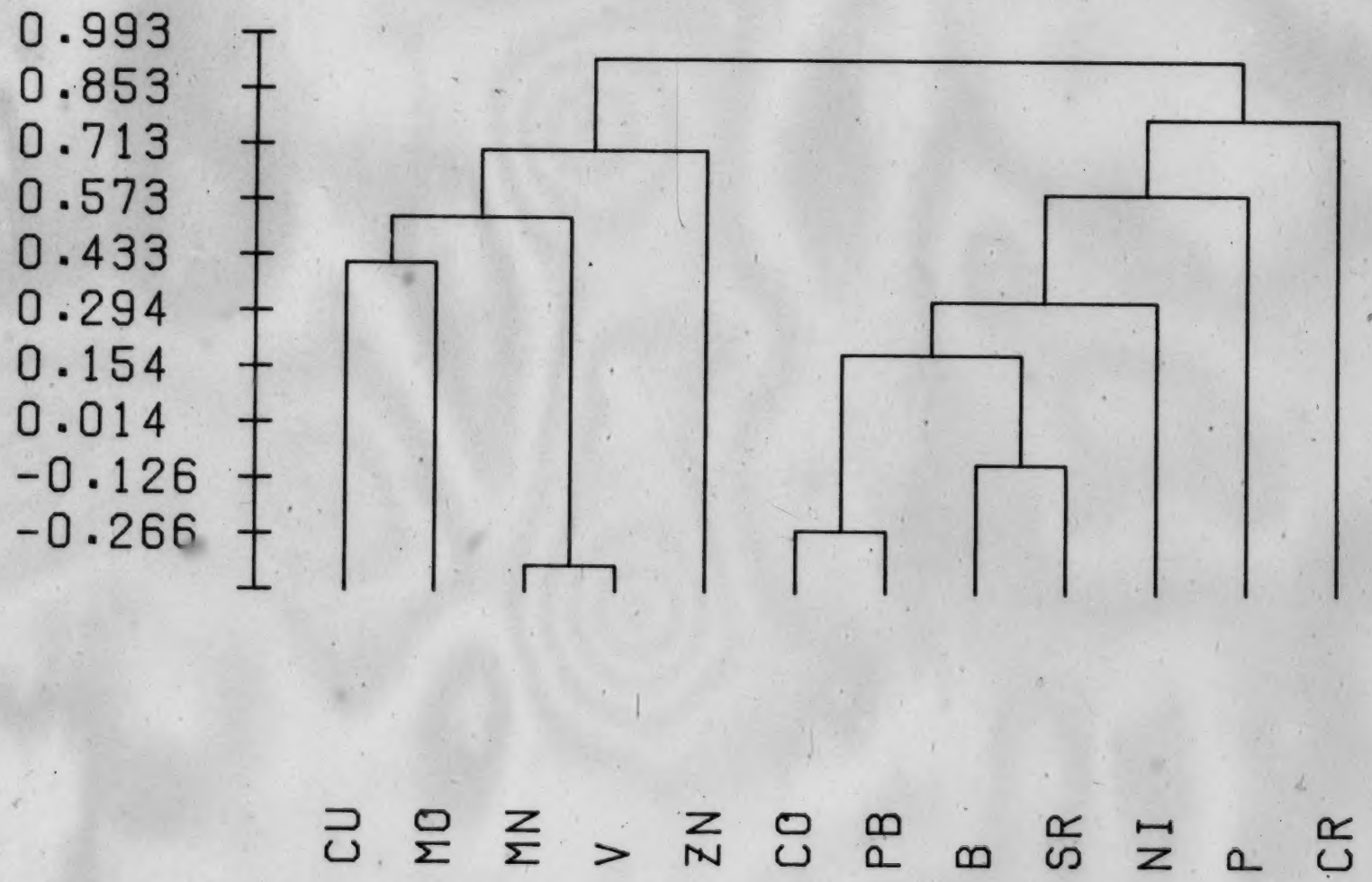

Figure 47. Dendrogram displaying the relationship between the minor elements in the clay separates from the study region.

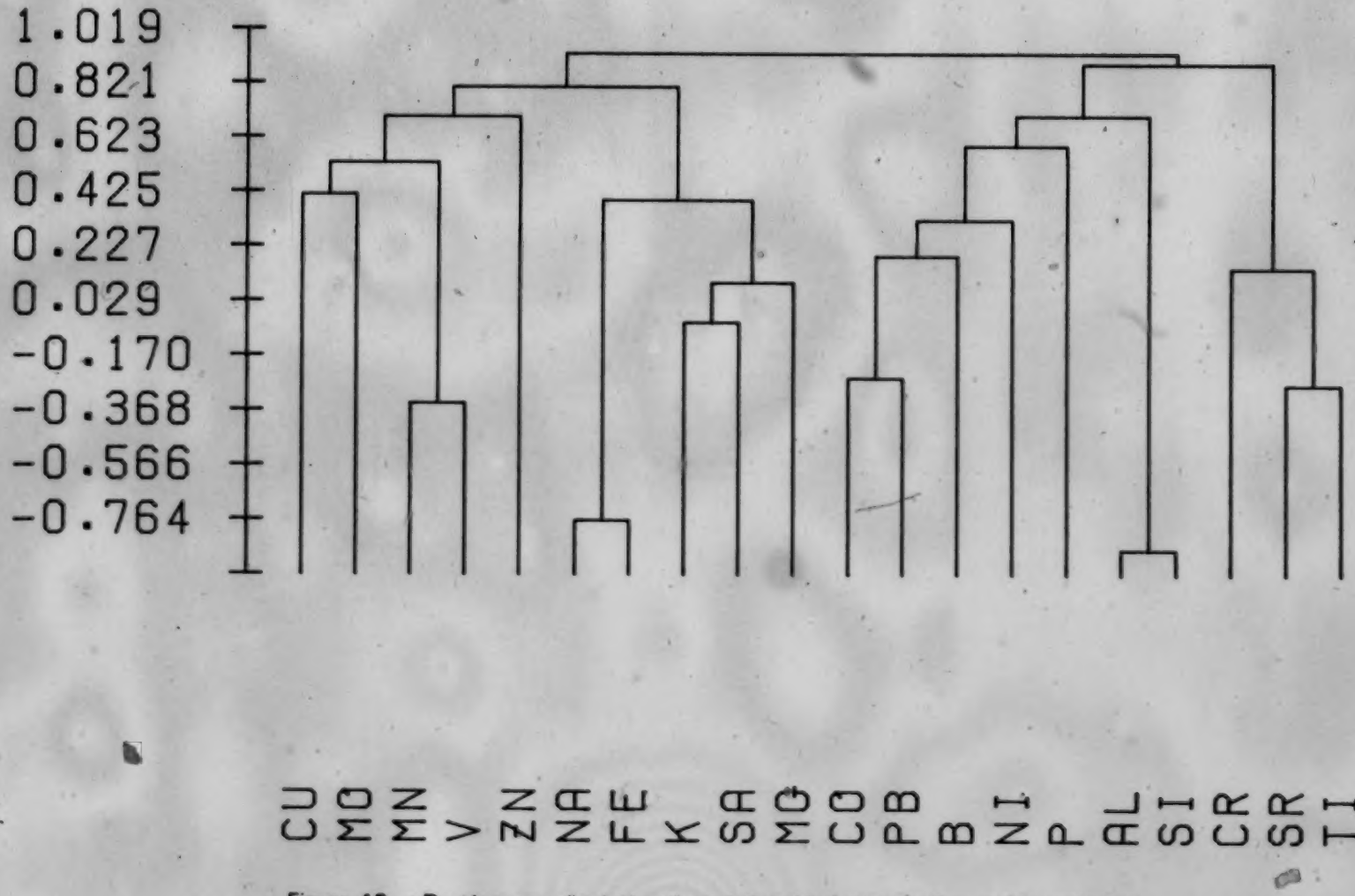

Figure 48. Dendrogram displaying the relationship between the major and minor elements in the clay separates from the study region

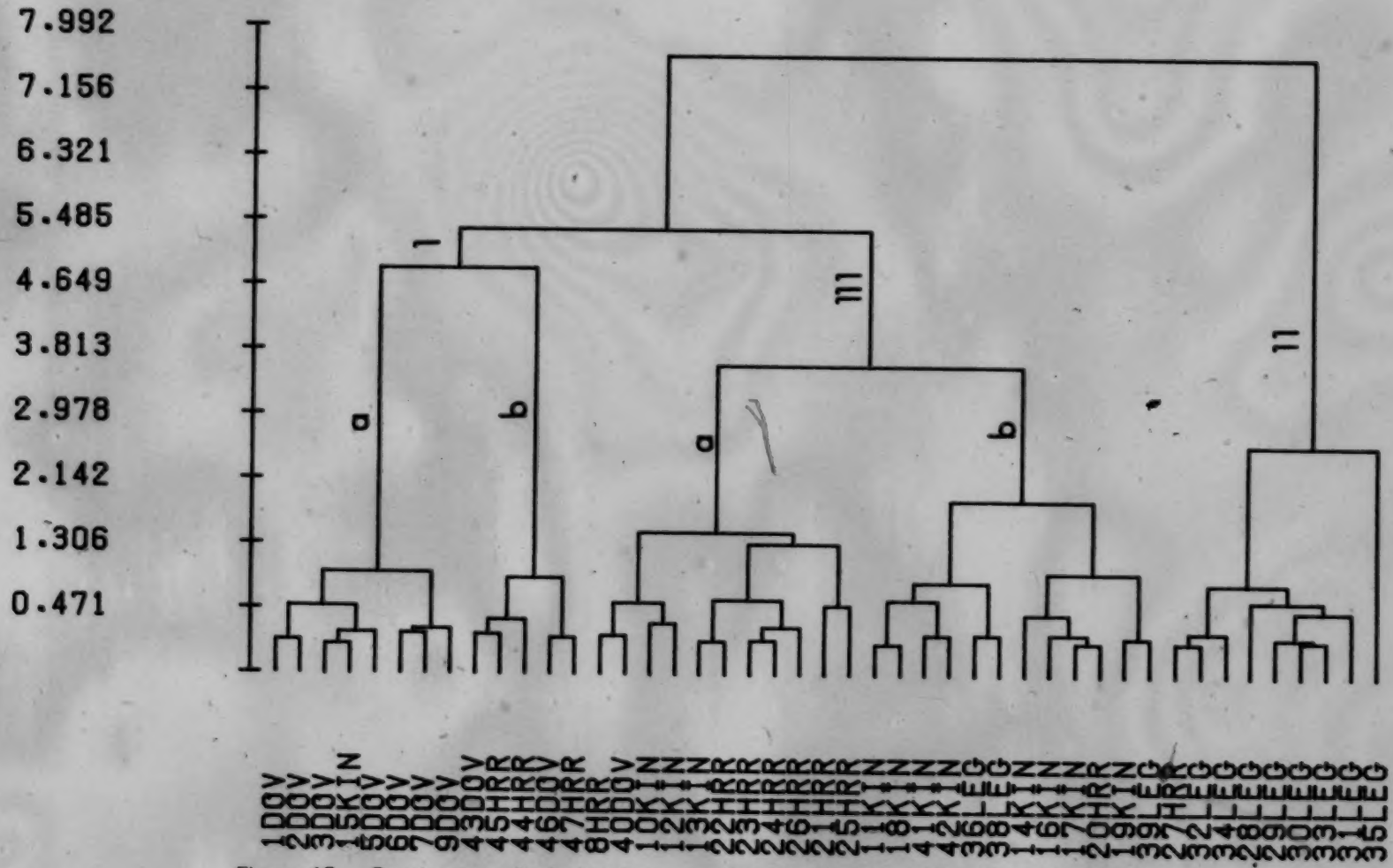

Figure 49. Dendrogram displaying the numerical classification of the clay separates from the study region based on the factor scores output from the P.C.A. of the chemical compositional data.

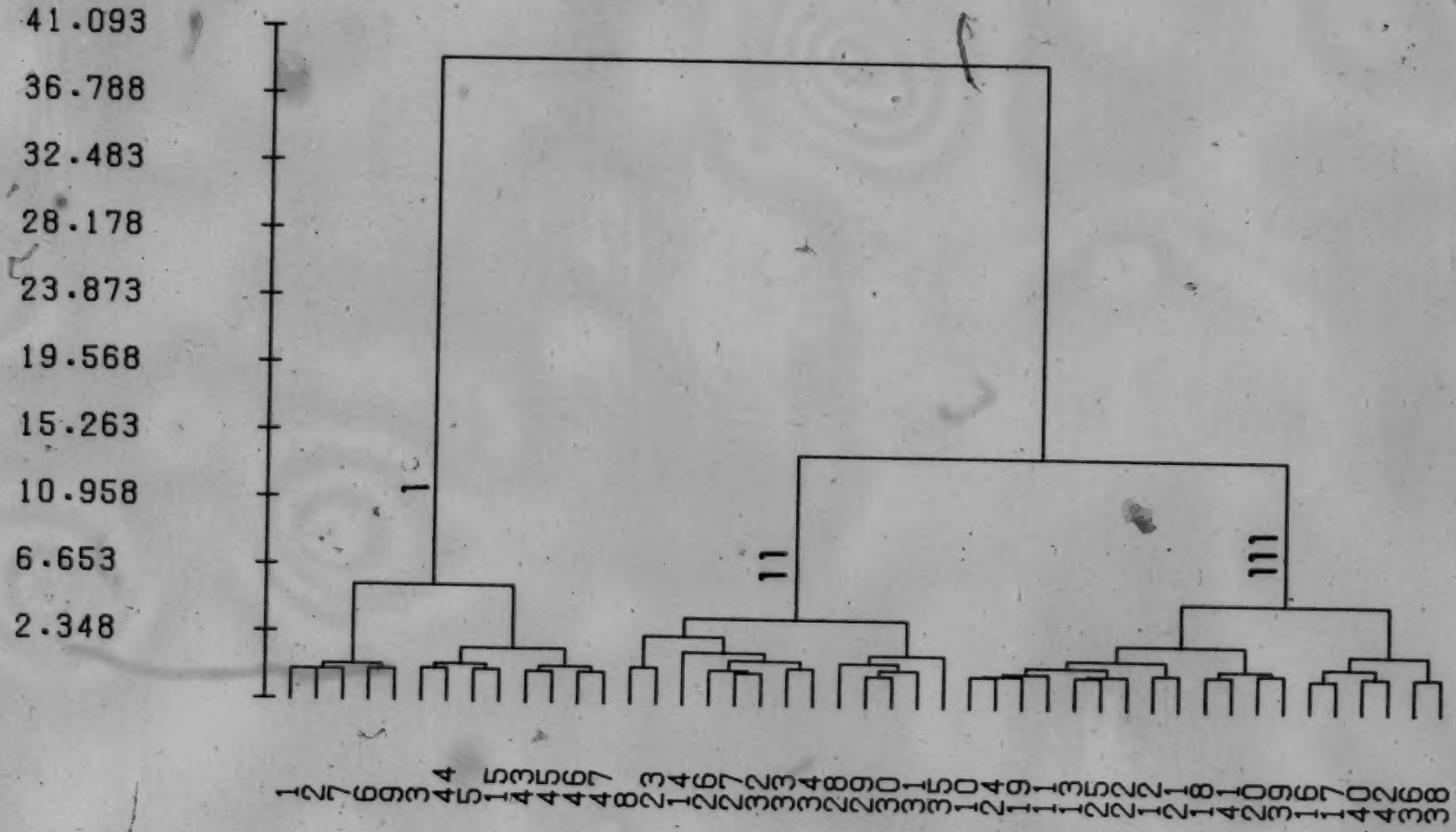

Figure 50. Dendrogram displaying the numerical classification of the clay separates from the study region based on the minor element composition.

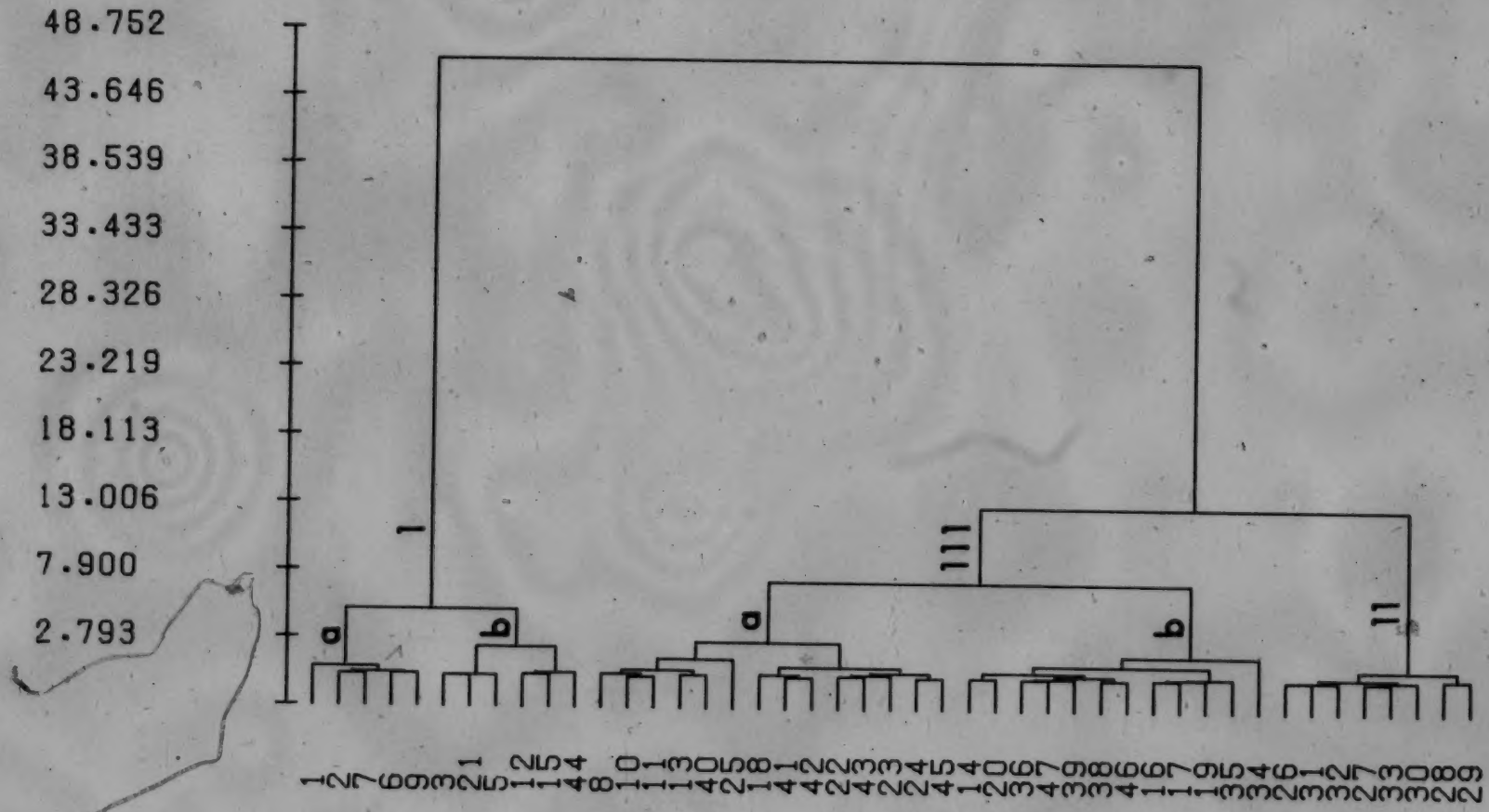

Figure 51. Dendrogram displaying the numerical classification of the clay separates from the study region based on the major element composition.

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APPENDICES

APPENDIX I.

Chemical composition of the parent material samples from the study area.

Sample Number	Cu	Co	Cr	Pb	Zn	Mn	V	Sr	Mo	P	Na	K	Ca	Mg	Fe	Al	Ni	Ti	pH	Hg	As	M.U.
1	28	12	51	25	47	199	84	184	1.3	576	0.50	1.44	0.99	0.82	2.15	5.61	32	0.29	7.9	25	2.5	1
2	16	13	47	19	39	221	80	171	1.0	524	0.44	1.31	2.00	0.82	2.01	5.07	29	0.26	7.5	24	3.4	1
3	22	5	60	19	62	218	115	120	1.3	735	0.54	1.53	2.36	1.28	2.15	5.34	36	0.32	7.6	45	6.0	1
4	22	7	64	21	76	393	130	156	3.4	901	0.59	1.32	1.18	0.79	3.01	5.91	38	0.36	7.4	44	9.0	1
5	23	9	53	20	50	287	103	128	1.8	521	0.51	1.36	0.48	0.63	2.41	5.75	45	0.31	7.0	37	5.0	1
6	17	13	49	25	34	238	80	146	1.7	434	0.29	1.04	0.45	0.54	2.12	5.15	37	0.30	7.4	27	2.5	1
7	16	10	37	17	29	178	67	141	1.1	444	0.35	0.97	2.87	0.87	1.63	4.12	22	0.26	4.4	24	2.1	1
8	23	6	55	18	65	292	109	166	2.1	815	0.61	1.59	3.11	1.10	3.02	5.86	35	0.28	7.7	44	6.5	3
9	16	8	37	17	30	185	67	140	1.3	446	0.35	0.99	2.92	0.88	1.64	4.14	23	0.24	8.1	20	2.5	1
10	11	7	26	10	24	165	43	89	0.5	266	0.45	0.86	0.32	0.26	1.38	3.02	16	0.15	5.1	20	2.1	2
11	10	16	30	15	27	174	54	95	1.2	207	0.47	0.94	0.30	0.32	1.54	3.57	16	0.18	4.6	22	2.1	2
12	13	3	31	13	32	176	57	85	0.8	397	0.30	0.89	4.43	1.14	1.60	3.46	19	0.18	5.0	22	2.9	2
13	13	27	29	18	24	181	46	92	1.0	237	0.41	0.91	0.29	0.29	1.39	3.26	13	0.17	5.6	22	2.1	2
14	17	17	34	22	40	224	66	90	2.5	325	0.44	0.99	0.31	0.34	1.89	3.71	21	0.19	4.7	23	5.5	2
15	17	19	41	21	38	251	68	103	1.4	450	0.37	1.18	3.74	1.12	1.88	4.52	25	0.25	7.0	32	2.9	2

FINE PRINT

Sample Number	Cu	Co	Cr	Pb	Zn	Mn	V	Sr	Mo	P	Na	K	Ca	Mg	Fe	Al	Ni	Ti	pH	Hg	As	M.U.
16	18	14	42	19	45	303	79	91	2.0	466	0.41	1.09	0.29	0.42	2.33	4.61	26	0.26	4.3	36	4.6	2
17	21	17	46	21	48	228	82	98	2.4	445	0.44	1.16	0.30	0.44	2.40	4.86	24	0.26	4.2	44	5.0	2
18	18	20	41	21	42	302	73	99	1.8	375	0.48	1.12	0.38	0.42	2.18	4.47	35	0.21	5.8	37	4.2	2
19	18	25	47	24	47	222	79	88	2.2	325	0.41	1.13	0.22	0.43	2.43	4.86	27	0.23	4.7	38	2.9	3
20	23	23	55	24	60	303	106	135	2.4	633	0.63	1.40	0.74	0.74	3.30	5.41	38	0.26	6.4	52	7.0	3
21	19	26	33	16	30	167	56	115	1.1	373	0.35	0.94	3.64	0.92	1.50	3.68	18	0.18	7.7	77	2.5	3
22	17	29	37	18	42	224	63	101	1.2	471	0.38	1.11	4.25	0.97	1.88	3.88	29	0.22	7.7	36	4.8	3
23	16	24	48	20	39	278	64	122	1.8	473	0.60	1.30	1.75	0.62	1.96	4.43	35	0.22	7.5	33	3.9	3
24	17	21	36	14	39	228	70	98	0.8	504	0.45	1.12	1.93	0.71	1.93	4.07	31	0.23	7.4	38	5.5	3
25	29	27	74	24	65	313	152	142	1.8	715	0.35	1.70	3.64	0.95	2.85	6.85	53	0.34	7.6	39	6.5	3
26	22	24	53	20	59	270	104	89	1.6	644	0.44	1.47	0.75	0.80	2.48	5.50	51	0.34	5.1	49	9.0	3
27	24	29	56	17	61	244	123	102	3.2	671	0.39	1.36	0.31	0.48	2.44	5.38	36	0.28	4.9	50	8.0	4
28	28	26	69	27	54	100	195	146	6.8	708	0.35	1.53	0.18	0.49	2.64	5.76	28	0.27	4.4	75	11.5	4
29	31	28	87	33	78	74	217	143	3.5	831	0.35	1.85	0.14	0.61	3.28	7.64	36	0.33	7.1	79	12.0	4
30	30	31	91	28	84	74	223	121	4.4	709	0.28	1.81	0.13	0.65	2.99	7.20	43	0.33	4.5	81	10.5	4

FINE PRINT

Sample Number	Cu	Co	Cr	Pb	Zn	Mn	V	Sr	Mo	P	Na	K	Ca	Mg	Fe	Al	Ni	Ti	pH	Hg	As	M.U.
31	24	31	67	26	74	382	163	98	4.1	733	0.39	1.38	0.35	0.56	2.76	5.76	46	0.31	5.9	64	10.0	4
32	18	23	50	16	53	290	106	92	1.2	551	0.41	1.15	0.39	0.46	2.22	4.82	26	0.24	3.8	42	7.0	4
33	31	33	90	23	99	839	215	100	4.3	917	0.32	1.76	0.26	0.72	5.16	7.51	45	0.38	3.7	89	11.5	4
34	18	27	50	20	53	322	108	107	2.6	574	0.45	1.20	0.36	0.42	2.28	4.79	28	0.23	4.4	43	7.0	4
35	19	24	49	20	55	239	104	99	2.3	563	0.44	1.19	0.38	0.45	2.26	4.78	33	0.21	5.3	48	7.5	4
36	19	5	68	19	50	268	116	111	1.8	458	0.51	1.33	0.41	0.48	2.36	5.20	38	0.22	4.7	42	7.0	4
38	25	3	69	23	61	152	161	128	3.2	785	0.40	1.62	0.22	0.53	2.95	6.25	28	0.27	4.4	57	10.0	4
39	17	8	45	20	44	451	75	96	1.7	443	0.47	1.11	0.35	0.42	2.28	4.61	38	0.20	5.3	34	4.6	4
40	20	5	42	16	47	212	73	95	1.4	537	0.46	1.05	3.12	1.26	1.76	4.04	25	0.21	3.7	42	4.6	1
41	16	4	44	19	44	262	77	83	1.8	443	0.38	1.14	0.30	0.43	2.13	4.74	24	0.23	3.8	37	4.6	2
42	17	2	44	18	40	277	78	86	1.5	430	0.42	1.11	0.32	0.44	2.13	4.78	25	0.21	3.9	30	3.8	2
43	16	14	43	10	46	287	86	127	0.1	410	0.44	1.29	0.39	0.49	2.36	5.05	39	0.23	5.2	31	4.1	1
44	15	11	37	10	38	209	73	129	0.0	474	0.38	1.16	4.34	1.06	2.00	4.70	29	0.22	7.5	45	5.3	3
45	19	13	41	12	49	318	87	127	0.4	631	0.49	1.43	2.52	0.71	2.56	5.34	31	0.22	7.3	45	5.3	3
46	19	14	40	9	47	288	85	106	0.7	475	0.49	1.21	0.87	0.58	2.86	5.01	31	0.19	7.4	31	4.1	1

FINE PRINT

Sample Number	Cu	Co	Cr	Pb	Zn	Mn	V	Sr	Mo	P	Na	K	Ca	Mg	Fe	Al	Ni	Tl	pH	Hg	As	M.U.
47	29	20	86	17	74	240	193	126	1.1	721	0.39	1.87	0.61	0.92	4.19	9.20	64	0.32	5.0	45	5.3	3
48	7	9	18	4	25	246	36	121	0.0	398	0.82	1.14	0.40	0.21	1.09	3.22	14	0.12	5.7			
49	14	15	36	15	38	248	67	94	0.7	435	0.44	1.18	1.58	0.83	1.91	4.17	28	0.24	7.3			
50	3	5	9	8	6	77	13	53	0.3	131	0.22	0.42	0.12	0.08	0.51	1.24	3	0.08	4.6			
51	49	21	99	29	91	92	316	205	5.3	971	0.37	2.14	0.17	0.87	3.56	8.64	42	0.38	3.8			
52	6	7	17	9	16	273	37	69	0.7	234	0.27	0.65	0.15	0.15	0.92	2.05	7	0.12	5.2			
53	2	4	5	7	6	55	11	57	0.4	109	0.31	0.43	0.13	0.06	0.39	1.18	3	0.05	4.6			
54	27	26	67	20	77	484	139	174	1.5	892	0.63	1.93	2.89	1.18	3.66	7.46	48	0.32	7.4			
55	2	2	4	7	3	22	6	43	0.3	72	0.14	0.22	0.07	0.03	0.15	0.57	3	0.05	4.7			
56	8	13	26	10	36	220	55	163	0.3	530	0.87	1.22	1.64	0.54	1.52	3.88	21	0.18	7.6			
57	29	26	74	22	92	476	149	140	1.8	853	0.49	2.03	2.29	1.28	3.40	7.98	60	0.32	7.2			
58	13	17	36	12	50	309	74	169	0.8	662	0.84	1.40	2.49	0.83	2.03	4.69	35	0.22	7.3			
59	18	20	44	16	61	402	92	154	1.1	771	0.73	1.53	2.02	0.87	2.51	5.34	34	0.24	7.7			
60	2	2	3	5	2	16	5	33	0.2	46	0.08	0.12	0.03	0.02	0.09	0.32	2	0.03	4.8			
61	3	5	6	8	7	88	11	83	0.1	168	0.37	0.62	0.21	0.08	0.48	1.43	5	0.05	5.1			

FINE PRINT

Sample Number	Cu	Co	Cr	Pb	Zn	Mn	V	Sr	Mo	P	Na	K	Ca	Mg	Fe	Al	Ni	Ti	pH
62	22	23	58	24	51	293	108	169	1.0	641	0.47	1.68	5.58	1.23	2.71	6.35	43	0.31	7.3
63	9	20	36	15	31	233	68	93	1.1	248	0.43	0.88	0.51	0.29	2.47	3.83	23	0.18	6.7
64	36	28	99	45	99	125	302	170	1.3	1201	0.23	2.63	0.34	0.95	3.91	9.99	73	0.41	4.7
65	25	19	54	25	44	86	109	127	3.6	730	0.28	1.26	0.16	0.50	2.95	5.35	28	0.24	3.9
66	4	8	14	13	9	85	20	57	0.7	130	0.16	0.53	0.13	0.14	0.80	1.60	7	0.12	5.3
67	3	3	5	11	3	21	6	37	0.7	71	0.13	0.21	0.06	0.03	0.16	0.56	3	0.05	4.8
68	9	15	28	18	19	105	46	88	0.9	201	0.21	0.84	0.20	0.35	1.72	3.57	19	0.16	4.6
69	5	4	9	5	12	73	20	62	1.0	162	0.28	0.73	0.13	0.09	0.59	1.55	3	0.10	5.1
70	11	11	34	5	31	214	61	132	0.1	453	0.38	1.21	1.45	0.60	2.00	4.28	29	0.22	6.9
71	1	2	3	1	4	59	7	47	0.1	95	0.20	0.32	0.09	0.04	0.36	0.79	3	0.05	4.9
72	2	3	8	1	10	104	14	67	0.1	181	0.30	0.42	0.17	0.10	0.70	1.36	5	0.07	5.1
73	5	7	22	2	23	109	49	105	0.1	333	0.55	0.99	0.31	0.23	1.47	3.26	12	0.06	5.0
75	4	4	8	1	12	185	16	109	0.1	183	0.49	0.79	8.24	1.44	1.27	1.94	6	0.07	7.6
76	5	5	19	4	11	134	26	121	0.1	300	0.18	0.76	4.02	2.04	1.20	2.69	6	0.13	7.3

FINE PRINT

Sample Number	Cu	Co	Cr	Pb	Zn	Mn	V	Sr	Mo	P	Na	K	Ca	Mg	Fe	Al	Ni	Ti	pH
78	14	16	69	9	48	244	119	151	0.1	467	0.58	1.87	0.41	0.75	3.59	7.69	30	0.27	4.3
79	5	5	15	1	17	125	23	70	0.1	252	0.34	0.60	0.28	0.15	0.93	1.80	3	0.10	6.5
80	5	7	19	2	26	187	38	116	0.1	391	0.71	1.09	0.36	0.20	1.13	3.17	9	0.18	5.8
81	17	17	50	13	39	216	85	119	0.1	303	0.34	1.18	0.27	0.54	2.63	5.48	28	0.20	4.1
82	10	9	37	9	26	119	64	108	0.1	237	0.27	0.93	0.24	0.39	1.80	4.08	16	0.21	4.6
84	10	16	38	9	33	382	69	102	0.1	422	0.48	1.00	1.39	0.81	3.29	4.13	25	0.20	7.5
85	16	16	45	12	43	241	82	84	0.1	313	0.31	1.06	0.36	0.47	2.95	4.75	31	0.22	5.0
86	14	14	40	11	35	243	76	103	0.1	244	0.35	0.99	0.37	0.42	2.27	4.48	27	0.21	5.2
87	17	15	41	12	35	229	71	105	0.1	322	0.39	0.97	0.38	0.43	2.18	4.24	23	0.19	5.5
90	5	5	14	4	11	89	22	58	0.1	138	0.18	0.65	0.16	0.19	0.86	1.97	3	0.11	6.4
91	6	5	15	8	13	126	26	71	0.1	193	0.22	0.72	2.66	1.08	0.99	2.19	13	0.12	5.9
92	20	15	49	11	60	307	102	112	0.5	685	0.50	1.58	1.51	0.78	2.92	6.06	38	0.26	7.3
93	26	15	54	28	53	368	104	156	1.1	692	0.85	1.56	1.67	1.02	2.73	5.65	28	0.27	7.7
94	11	5	13	18	4	112	26	65	0.1	207	0.29	0.55	4.41	1.97	0.80	1.60	10	0.17	7.5
95	20	11	39	23	29	198	75	114	0.2	483	0.45	1.03	4.39	1.21	1.91	4.09	30	0.27	7.8

FINE PRINT

Sample Number	Cu	Co	Cr	Pb	Zn	Mn	V	Sr	Mo	P	Na	K	Ca	Mg	Fe	Al	Ni	Ti	pH
97	6	2	3	18	1	17	6	31	0.1	56	0.09	0.11	0.04	0 02	0.11	0.34	3	0.02	5.8
98	8	6	10	17	4	103	20	97	0.2	159	0.60	0.99	0.37	0.14	1.16	2.29	10	0.10	6.6
99	22	13	42	30	45	216	89	89	0.2	525	0.42	1.28	0.73	0.52	2.06	4.35	29	0.22	6.5
100	17	12	43	31	22	201	76	100	0.3	328	0.46	1.17	0.37	0.44	2.17	4.72	27	0.21	5.0
101	24	17	48	33	48	608	97	156	1.4	711	0.87	1.44	1.19	0.55	2.40	5.29	25	0.20	6.4

Summary Statistics

	Cu	Co	Cr	Pb	Zn	Mn	V	Sr	Mo	P	Na	K	Ca	Mg	Fe	Al	Ni	Ti	pH
Mean	16	14	41	16	40	222	83	109	1.2	458	0.42	1.14	1.24	0.62	2.04	4.38	26	0.21	5.9
Stand. Dev.	8	8	22	8	23	127	58	35	1.3	240	0.16	0.45	1.54	0.40	0.97	1.97	14	0.09	1.3
Skewness	0.5	0.3	0.4	0.3	0.4	1.5	1.6	0.1	1.7	0.4	0.7	0.2	1.8	0.9	0.1	0.09	0.3	-0.3	0.1
Kurtosis	0.8	-1	.04	0.5	-0.1	5.4	3.7	-0.1	3.8	-0.1	1.1	0.8	4.01	0.4	0.4	0.3	0.4	-0.3	-1.4

**Values for Na, K, Ca, Fe, Mg, Al and Si expressed as %, Hg expressed as ppb. All other elements as ug gm
M.U. Indicates Soil Unit Membership: 1. Dover, 2. Kinosis, 3. Horse River, 4. Legend

FINE PRINT

FINE PRINT

APPENDIX II.

Chemical Composition of the Clay Separates from the Major Soil Units of the Study Area.

Sample Number	Cu	Co	B	Cr	Pb	Zn	Mn	V	Sr	Mo	P	Na	Ca	K	Mg	Fe	Al	CEC	KEC	SA	Ti	Ni	Si	M.U.
1	38	14	218	75	42	71	182	126	276	1.3	744	0.43	1.03	2.05	0.88	3.34	8.38	40	27	286	0.27	51	34.01	1
2	40	14	188	75	38	66	165	124	310	1.5	702	0.37	1.96	1.87	0.91	3.31	8.06	46	33	305	0.26	53	33.83	1
3	51	18	214	97	40	108	210	186	315	2.2	875	0.36	1.36	2.29	1.30	4.24	9.74	41	32	345	0.30	68	31.54	1
4	53	16	205	96	40	95	220	168	320	1.6	850	0.33	1.11	2.09	0.92	4.16	8.39	35	31	385	0.29	72	32.13	1
5	59	23	197	95	41	104	335	198	364	3.5	915	0.35	1.14	2.10	1.06	4.69	9.94	40	32	405	0.31	70	31.50	1
6	47	17	160	80	45	62	182	134	409	1.8	678	0.32	0.91	1.65	0.84	3.63	8.81	37	32	340	0.28	64	33.84	1
7	42	15	149	71	39	63	178	126	353	1.5	707	0.34	0.95	1.75	0.82	3.09	8.19	31	28	275	0.28	56	34.67	1
9	58	18	185	73	36	68	175	143	398	2.1	773	0.35	3.40	1.72	1.02	3.61	8.29	48	35	274	0.29	59	32.47	1
40	105	19	198	113	44	164	367	270	145	4.2	1089	0.33	2.49	2.17	1.48	5.92	10.87	61	45	590	0.34	105	28.58	1
43	45	17	228	102	42	103	257	189	116	4.0	760	0.23	0.73	1.96	0.97	5.84	11.23	45	44	463	0.33	67	30.08	1
46	48	17	255	119	43	119	332	218	102	4.9	963	0.23	1.09	2.28	1.18	6.56	12.12	48	47	418	0.38	66	28.18	1
10	94	19	298	118	59	132	324	223	177	4.1	933	0.28	1.01	2.18	1.11	6.43	11.40	43	27	445	0.36	89	29.05	2
11	81	19	160	119	52	115	310	233	338	4.0	791	0.27	0.93	2.15	1.13	6.32	11.81	40	31	438	0.36	73	28.84	2
12	72	16	115	96	40	150	240	192	211	3.2	909	0.21	1.31	2.11	1.27	4.82	9.84	41	34	479	0.33	72	31.29	2
13	111	17	284	107	54	122	284	206	303	3.9	819	0.30	0.83	2.24	1.08	5.53	10.76	50	28	431	0.37	81	30.31	2
14	107	27	259	128	46	196	374	252	318	7.6	983	0.25	1.20	2.14	1.14	7.87	12.37	37	32	484	0.37	108	27.12	2
15	66	20	209	86	38	103	374	175	291	2.9	813	0.25	3.51	1.94	1.17	4.59	9.45	37	28	458	0.31	70	30.52	2
16	93	18	213	118	58	147	349	251	336	6.7	1254	0.18	1.01	1.97	1.15	7.56	12.96	47	31	458	0.37	86	27.03	2
17	88	16	226	130	45	161	348	276	371	6.6	1258	0.21	1.12	2.12	1.23	7.34	13.05	39	38	487	0.35	86	26.87	2
18	86	19	270	114	31	131	336	235	334	2.0	671	0.16	0.81	1.93	0.84	6.41	11.21	39	34	490	0.36	100	29.82	2

FINE PRINT

Sample Number	Cu	Co	B	Cr	Pb	Zn	Mn	V	Sr	Mo	P	Na	Ca	K	Mg	Fe	Al	CEC	KEC	SA	Ti	Ni	Si	M.U.
19	88	18	281	125	49	146	275	272	216	4.6	977	0.15	0.77	1.99	1.23	7.42	13.40	37	35	447	0.37	86	26.87	2
41	86	15	256	113	42	136	280	240	424	3.7	1108	0.19	1.38	2.23	1.10	6.18	11.99	62	57	525	0.35	99	28.48	2
42	111	16	210	115	49	134	287	246	413	5.7	1050	0.19	1.32	1.97	1.12	6.49	11.84	59	58	560	0.35	105	28.58	2
20	74	14	224	129	49	167	289	280	353	4.3	1038	0.24	1.26	2.31	1.36	7.48	11.66	40	40	438	0.36	98	27.70	3
21	103	17	295	95	50	155	278	196	295	2.8	953	0.36	1.34	2.25	1.34	4.71	9.31	40	35	390	0.31	64	31.60	3
22	96	18	289	108	48	141	324	217	337	3.6	1035	0.23	1.28	2.14	1.42	5.89	10.11	49	32	437	0.33	82	30.20	3
23	94	28	176	120	44	149	368	243	314	3.7	1010	0.25	3.21	1.97	1.06	6.67	10.22	61	33	463	0.34	71	28.68	3
24	89	21	254	115	45	143	415	245	349	4.6	1102	0.22	2.84	2.21	1.25	6.37	11.09	61	34	463	0.33	87	28.09	3
25	113	19	251	110	37	114	291	249	337	3.0	1019	0.30	4.61	3.31	1.18	4.74	10.91	67	35	396	0.26	79	27.63	3
26	89	27	333	125	46	168	271	261	322	4.8	1077	0.20	1.13	3.86	1.26	6.59	12.40	60	32	520	0.30	109	27.00	3
27	96	25	295	123	46	165	228	310	327	3.6	1382	0.21	0.94	3.33	1.08	6.23	12.35	40	35	484	0.31	102	27.80	3
44	47	17	219	100	51	90	240	169	165	2.8	795	0.26	4.05	2.01	1.13	4.76	10.40	59	40	384	0.30	56	29.22	3
45	47	18	250	106	39	112	338	197	128	4.5	1000	0.22	4.55	2.16	1.03	5.69	11.03	63	47	369	0.33	64	27.69	3
47	51	17	278	126	44	120	229	247	92	4.7	970	0.20	0.97	2.21	1.13	6.72	12.79	50	49	463	0.35	74	27.68	3
8	98	32	195	114	41	165	353	245	194	2.4	989	0.26	1.57	2.58	1.28	5.73	11.87	36	27	386	0.36	90	28.39	3
28	105	24	230	140	39	126	150	473	423	4.6	1795	0.28	0.57	3.76	1.04	6.67	11.67	36	29	480	0.30	75	28.06	4
29	95	28	253	149	38	155	104	409	331	3.8	1298	0.28	0.51	3.92	1.10	6.47	13.12	35	34	495	0.33	92	26.85	4
30	95	28	253	149	38	155	104	409	331	3.8	1298	0.20	0.60	3.77	1.02	5.73	12.36	35	33	501	0.32	92	28.16	4
31	104	25	281	141	41	189	240	403	362	3.7	1503	0.22	1.16	3.80	1.11	6.39	12.32	34	32	523	0.29	106	27.29	4
32	94	26	190	132	48	178	290	333	372	3.6	1428	0.21	1.16	3.62	1.11	6.62	11.92	50	49	583	0.29	110	27.60	4

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Sample Number	Cu	Co	B	Cr	Pb	Zn	Mn	V	Sr	Mo	P	Na	Ca	K	Mg	Fe	Al	CEC	KEC	SA	Ti	Ni	Si	M.U.
33	69	26	210	145	42	190	198	391	320	5.2	1310	0.20	1.00	3.36	1.08	5.98	12.50	50	49	539	0.29	105	27.81	4
34	90	30	241	129	42	169	265	344	386	6.1	1506	0.22	1017	2.35	1.03	6.49	11.84	51	50	581	0.29	104	22.64	4
35	80	33	261	174	35	162	88	504	306	5.3	1511	0.18	0.53	2.46	1.06	7.86	13.45	53	53	575	0.23	96	26.59	4
36	76	14	199	138	45	189	192	353	353	5.8	1471	0.20	1.11	2.13	1.12	7.11	12.28	55	52	580	0.33	125	27.79	4
38	88	15	291	139	49	151	222	362	410	6.7	1058	0.23	1.49	2.33	1.15	6.64	12.21	48	48	569	0.34	112	27.80	4
39	81	15	221	124	47	146	328	255	278	3.8	1136	0.17	1.09	2.03	1.19	7.14	12.43	57	56	550	0.33	126	27.71	4

Summary Statistics

	Cu	Co	B	Cr	Pb	Zn	Mn	V	Sr	Mo	P	Na	Ca	K	Mg	Fe	Al	CEC	KEC	SA	Ti	Ni	Si
Mean	79	20	231	115	44	135	265	256	303	3.9	1050	0.25	1.71	2.41	1.12	5.87	11.18	46	38	456	0.32	85	29
Stand. Dev.	22	5	46	22	6	36	79	90	88	1.5	262	0.1	1.65	0.65	0.15	1.27	1.51	10	9	84	0.04	20	2.3
Skewness	-0.4	0.9	-0.2	-0.03	0.5	-0.4	-0.4	0.9	-1.0	0.3	0.8	0.7	3.5	1.4	0.1	-0.6	-0.6	0.5	0.8	-0.4	-0.4	0.2	0.5
Kurtosis	-1.2	-0.3	-0.1	0.2	0.5	-0.5	-0.5	0.5	0.2	-0.2	0.2	-0.1	15	0.6	0.3	-0.4	-0.6	-0.9	-0.6	-0.3	-0.4	-0.9	0.8

**Values for Na, K, Ca, Fe, Mg, Al and Si expressed as %.

All other elements as ug. gm^{-1}.

M.U. Indicates Soil Unit Membership. 1. Dover
2. Kinosis
3. Horse River
4. Legend

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APPENDIX III.

Analyses of Variance of the Chemical Compositional Data for the Major Soil Units.

FINE PRINT

ANALYSIS OF VARIANCE OF THE CHEMICAL COMPOSITIONAL DATA FOR THE MAJOR SOIL UNITS

VARIABLE Cu
BY VARIABLE GROUP

ANALYSIS OF VARIANCE

SOURCE	D.F.	SUM OF SQUARES	MEAN SQUARES	F RATIO
BETWEEN GROUPS	3	387.5287	129.1762	6.542
WITHIN GROUPS	42	828.2798	19.7448	
TOTAL	45	1215.8083		

VARIABLE Co
BY VARIABLE GROUP

ANALYSIS OF VARIANCE

SOURCE	D.F.	SUM OF SQUARES	MEAN SQUARES	F RATIO
BETWEEN GROUPS	3	1093.7834	364.5945	5.681
WITHIN GROUPS	42	2694.4604	64.1776	
TOTAL	45	3788.2437		

VARIABLE As
BY VARIABLE GROUP

ANALYSIS OF VARIANCE

SOURCE	D.F.	SUM OF SQUARES	MEAN SQUARES	F RATIO
BETWEEN GROUPS	3	202.0814	67.3538	19.411
WITHIN GROUPS	42	145.7312	3.4698	
TOTAL	45	347.7525		

VARIABLE Cr
BY VARIABLE GROUP

ANALYSIS OF VARIANCE

SOURCE	D.F.	SUM OF SQUARES	MEAN SQUARES	F RATIO
BETWEEN GROUPS	3	4848.1944	1616.0647	9.383
WITHIN GROUPS	42	7249.2852	172.6020	
TOTAL	45	12097.4796		

VARIABLE Pb
BY VARIABLE GROUP

ANALYSIS OF VARIANCE

SOURCE	D.F.	SUM OF SQUARES	MEAN SQUARES	F RATIO
BETWEEN GROUPS	3	197.5207	65.8402	3.018
WITHIN GROUPS	42	916.3101	21.8169	
TOTAL	45	1113.8308		

VARIABLE Zn
BY VARIABLE GROUP

ANALYSIS OF VARIANCE

SOURCE	D.F.	SUM OF SQUARES	MEAN SQUARES	F RATIO
BETWEEN GROUPS	3	4316.0496	1438.3498	7.794
WITHIN GROUPS	42	7758.3979	184.6761	
TOTAL	45	12074.4453		

VARIABLE Mn
BY VARIABLE GROUP

ANALYSIS OF VARIANCE

SOURCE	D.F.	SUM OF SQUARES	MEAN SQUARES	F RATIO
BETWEEN GROUPS	3	19978.9944	6659.6641	0.482
WITHIN GROUPS	42	580593.4453	13823.6533	
TOTAL	45	600572.4375		

VARIABLE V
BY VARIABLE GROUP

ANALYSIS OF VARIANCE

SOURCE	D.F.	SUM OF SQUARES	MEAN SQUARES	F RATIO
BETWEEN GROUPS	3	45322.0291	15107.3398	11.847
WITHIN GROUPS	42	53557.1638	1275.1709	
TOTAL	45	98879.1875		

VARIABLE Sr
BY VARIABLE GROUP

ANALYSIS OF VARIANCE

SOURCE	D.F.	SUM OF SQUARES	MEAN SQUARES	F RATIO
BETWEEN GROUPS	3	12981.8374	4327.2773	11.418
WITHIN GROUPS	42	15920.5469	379.0606	
TOTAL	45	28902.3828		

VARIABLE Mo
BY VARIABLE GROUP

ANALYSIS OF VARIANCE

SOURCE	D.F.	SUM OF SQUARES	MEAN SQUARES	F RATIO
BETWEEN GROUPS	3	30.2988	10.0996	10.026
WITHIN GROUPS	42	42.30001.0071		
TOTAL	45	72.5988		

VARIABLE P
BY VARIABLE GROUP

ANALYSIS OF VARIANCE

SOURCE	D.F.	SUM OF SQUARES	MEAN SQUARES	F RATIO
BETWEEN GROUPS	3	575040.3288	191680.0825	10.982
WITHIN GROUPS	42	733048.2500	17453.4405	
TOTAL	45	1308088.0000		

VARIABLE Na
BY VARIABLE GROUP

ANALYSIS OF VARIANCE

SOURCE	D.F.	SUM OF SQUARES	MEAN SQUARES	F RATIO
BETWEEN GROUPS	3	0.0313	0.0104	1.632
WITHIN GROUPS	42	0.2889	0.0064	
TOTAL	45	0.0303		

VARIABLE Ca
BY VARIABLE GROUP

ANALYSIS OF VARIANCE

SOURCE	D.F.	SUM OF SQUARES	MEAN SQUARES	F RATIO
BETWEEN GROUPS	3	30.1780	10.0593	7.577
WITHIN GROUPS	42	55.78281.3277		
TOTAL	45	85.9408		

VARIABLE K
BY VARIABLE GROUP

ANALYSIS OF VARIANCE

SOURCE	D.F.	SUM OF SQUARES	MEAN SQUARES	F RATIO
BETWEEN GROUPS	31.1000	0.3667	7.287	
WITHIN GROUPS	42	2.0821	0.0496	
TOTAL	45	3.1821		

VARIABLE Mg
BY VARIABLE GROUP

ANALYSIS OF VARIANCE

SOURCE	D.F.	SUM OF SQUARES	MEAN SQUARES	F RATIO
BETWEEN GROUPS	31.2333	0.4111	8.544	
WITHIN GROUPS	42	2.0206	0.0481	
TOTAL	45	3.2542		

VARIABLE Fe
BY VARIABLE GROUP

ANALYSIS OF VARIANCE

SOURCE	D.F.	SUM OF SQUARES	MEAN SQUARES	F RATIO
BETWEEN GROUPS	3	5.03781.6783	4.103	
WITHIN GROUPS	42	17.1805	0.4093	
TOTAL	45	22.2283		

VARIABLE Al
BY VARIABLE GROUP

ANALYSIS OF VARIANCE

SOURCE	D.F.	SUM OF SQUARES	MEAN SQUARES	F RATIO
BETWEEN GROUPS	3	17.5168	5.8389	5.079
WITHIN GROUPS	42	48.28291.1498		
TOTAL	45	65.7998		

VARIABLE Si
BY VARIABLE GROUP

ANALYSIS OF VARIANCE

SOURCE	D.F.	SUM OF SQUARES	MEAN SQUARES	F RATIO
BETWEEN GROUPS	3	1555.3513	518.4504	6.785
WITHIN GROUPS	42	3209.1040	76.4072	
TOTAL	45	4764.4831		

VARIABLE Ti
BY VARIABLE GROUP

ANALYSIS OF VARIANCE

SOURCE	D.F.	SUM OF SQUARES	MEAN SQUARES	F RATIO
BETWEEN GROUPS	3	0.0301	0.0100	3.978
WITHIN GROUPS	42	0.1058	0.0025	
TOTAL	45	0.1359		

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VARIABLE Hg
BY VARIABLE GROUP

ANALYSIS OF VARIANCE

SOURCE	D.F.	SUM OF SQUARES	MEAN SQUARES	F RATIO
BETWEEN GROUPS	3	6280.1405	2093.3801	13.228
WITHIN GROUPS	42	6648.7322	158.2555	
TOTAL	45	12928.8711		

FINE PRINT

APPENDIX IV.

Analyses of Variance of the Clay Separate Mineralogical Data from the Major Soil Units.

FINE PRINT

ANALYSIS OF VARIANCE OF CLAY MINERALOGICAL COMPOSITIONAL DATA

VARIABLE MICA
BY VARIABLE GROUP

ANALYSIS OF VARIANCE

SOURCE	D.F.	SUM OF SQUARES	MEAN SQUARES	F RATIO
BETWEEN GROUPS	3	1045.7170	348.5723	15.182
WITHIN GROUPS	42	964.3197	22.9600	
TOTAL	45	2010.0386		

VARIABLE PAR
BY VARIABLE GROUP

ANALYSIS OF VARIANCE

SOURCE	D.F.	SUM OF SQUARES	MEAN SQUARES	F RATIO
BETWEEN GROUPS	3	25.8877	8.6293	20.155
WITHIN GROUPS	42	17.9817	0.4281	
TOTAL	45	43.8694		

VARIABLE VERMICULITE
BY VARIABLE GROUP

ANALYSIS OF VARIANCE

SOURCE	D.F.	SUM OF SQUARES	MEAN SQUARES	F RATIO
BETWEEN GROUPS	3	256.1802	85.0601	4.800
WITHIN GROUPS	42	785.8426	18.7105	
TOTAL	45	1044.0228		

VARIABLE TOTAL MICA
BY VARIABLE GROUP

ANALYSIS OF VARIANCE

SOURCE	D.F.	SUM OF SQUARES	MEAN SQUARES	F RATIO
BETWEEN GROUPS	3	872.1183	290.7061	12.302
WITHIN GROUPS	42	992.6316	23.6317	
TOTAL	45	1864.8498		

VARIABLE SMECTITE
BY VARIABLE GROUP

ANALYSIS OF VARIANCE

SOURCE	D.F.	SUM OF SQUARES	MEAN SQUARES	F RATIO
BETWEEN GROUPS	3	319.7852	106.5934	2.039
WITHIN GROUPS	42	2196.1677	52.2897	
TOTAL	45	2515.9529		

VARIABLE SMECTITE BY SURFACE AREA
BY VARIABLE GROUP

ANALYSIS OF VARIANCE

SOURCE	D.F.	SUM OF SQUARES	MEAN SQUARES	F RATIO
BETWEEN GROUPS	3	790.2863	263.4219	11.117
WITHIN GROUPS	42	995.2518	23.6965	
TOTAL	45	1785.5181		

VARIABLE SMECTITE BY KEC
BY VARIABLE GROUP

ANALYSIS OF VARIANCE

SOURCE	D.F.	SUM OF SQUARES	MEAN SQUARES	F RATIO
BETWEEN GROUPS	3	344.5308	114.8436	2.158
WITHIN GROUPS	42	2236.8345	53.2579	
TOTAL	45	2581.3652		

VARIABLE KAOLIN
BY VARIABLE GROUP

ANALYSIS OF VARIANCE

SOURCE	D.F.	SUM OF SQUARES	MEAN SQUARES	F RATIO
BETWEEN GROUPS	3	1315.1812	438.3870	7.870
WITHIN GROUPS	42	2339.0828	55.7082	
TOTAL	45	3654.8237		

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APPENDIX V.

Analyses of Variance of the Clay Separate Chemical Compositional Data for the Major Soil Units.

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ANALYSIS OF VARIANCE OF CLAY COMPOSITIONAL DATA

VARIABLE Cu
BY VARIABLE GROUP

ANALYSIS OF VARIANCE

SOURCE	D.F.	SUM OF SQUARES	MEAN SQUARES	F RATIO
BETWEEN GROUPS	3	10058.2542	3352.7512	11.113
WITHIN GROUPS	42	12670.9761	301.6887	
TOTAL	45	22729.2266		

VARIABLE Co
BY VARIABLE GROUP

ANALYSIS OF VARIANCE

SOURCE	D.F.	SUM OF SQUARES	MEAN SQUARES	F RATIO
BETWEEN GROUPS	3	315.9661	105.3220	4.734
WITHIN GROUPS	42	934.4919	22.2498	
TOTAL	45	1250.4580		

VARIABLE S
BY VARIABLE GROUP

ANALYSIS OF VARIANCE

SOURCE	D.F.	SUM OF SQUARES	MEAN SQUARES	F RATIO
BETWEEN GROUPS	3	15312.2016	5104.0684	3.412
WITHIN GROUPS	42	75132.2109	1788.8621	
TOTAL	45	83444.3750		

VARIABLE Cr
BY VARIABLE GROUP

ANALYSIS OF VARIANCE

SOURCE	D.F.	SUM OF SQUARES	MEAN SQUARES	F RATIO
BETWEEN GROUPS	3	14505.5717	4835.2227	26.589
WITHIN GROUPS	42	7643.5286	181.9887	
TOTAL	45	22148.1953		

VARIABLE Pb
BY VARIABLE GROUP

ANALYSIS OF VARIANCE

SOURCE	D.F.	SUM OF SQUARES	MEAN SQUARES	F RATIO
BETWEEN GROUPS	3	254.4652	84.8217	2.851
WITHIN GROUPS	42	1249.4613	29.7491	
TOTAL	45	1503.9265		

VARIABLE Zn
BY VARIABLE GROUP

ANALYSIS OF VARIANCE

SOURCE	D.F.	SUM OF SQUARES	MEAN SQUARES	F RATIO
BETWEEN GROUPS	3	29632.2281	9877.4063	14.913
WITHIN GROUPS	42	27817.8555	662.3298	
TOTAL	45	57450.0781		

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VARIABLE Mn
BY VARIABLE GROUP

ANALYSIS OF VARIANCE

SOURCE	D.F.	SUM OF SQUARES	MEAN SQUARES	F RATIO
BETWEEN GROUPS	3	104357.8281	34785.9414	8.220
WITHIN GROUPS	42	177739.5977	4231.8943	
TOTAL	45	282097.3760		

VARIABLE V
BY VARIABLE GROUP

ANALYSIS OF VARIANCE

SOURCE	D.F.	SUM OF SQUARES	MEAN SQUARES	F RATIO
BETWEEN GROUPS	3	272514.7502	90838.2500	40.347
WITHIN GROUPS	42	94560.9414	2251.4503	
TOTAL	45	367075.6875		

VARIABLE Sr
BY VARIABLE GROUP

ANALYSIS OF VARIANCE

SOURCE	D.F.	SUM OF SQUARES	MEAN SQUARES	F RATIO
BETWEEN GROUPS	3	46889.8890	15563.2266	2.120
WITHIN GROUPS	42	308344.7988	7341.5381	
TOTAL	45	355034.4375		

VARIABLE Mo
BY VARIABLE GROUP

ANALYSIS OF VARIANCE

SOURCE	D.F.	SUM OF SQUARES	MEAN SQUARES	F RATIO
BETWEEN GROUPS	3	32.6885	10.8962	8.820
WITHIN GROUPS	42	68.12881.5459		
TOTAL	45	101.8172		

VARIABLE P
BY VARIABLE GROUP

ANALYSIS OF VARIANCE

SOURCE	D.F.	SUM OF SQUARES	MEAN SQUARES	F RATIO
BETWEEN GROUPS	3	1946932.2744	648977.3750	23.972
WITHIN GROUPS	42	1137016.3750	27071.8184	
TOTAL	45	3083948.0000		

VARIABLE Na
BY VARIABLE GROUP

ANALYSIS OF VARIANCE

SOURCE	D.F.	SUM OF SQUARES	MEAN SQUARES	F RATIO
BETWEEN GROUPS	3	0.0945	0.0315	13.779
WITHIN GROUPS	42	0.0960	0.0023	
TOTAL	45	0.1905		

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VARIABLE Ca
BY VARIABLE GROUP

ANALYSIS OF VARIANCE

SOURCE	D.F.	SUM OF SQUARES	MEAN SQUARES	F RATIO
BETWEEN GROUPS	3	7.3782	2.4594	0.901
WITHIN GROUPS	42	114.6424	2.7295	
TOTAL	45	122.0206		

VARIABLE K
BY VARIABLE GROUP

ANALYSIS OF VARIANCE

SOURCE	D.F.	SUM OF SQUARES	MEAN SQUARES	F RATIO
BETWEEN GROUPS	3	7.8550	2.6183	10.119
WITHIN GROUPS	42	10.8674	0.2587	
TOTAL	45	18.7224		

VARIABLE Mg
BY VARIABLE GROUP

ANALYSIS OF VARIANCE

SOURCE	D.F.	SUM OF SQUARES	MEAN SQUARES	F RATIO
BETWEEN GROUPS	3	0.1877	0.0626	3.438
WITHIN GROUPS	42	0.7665	0.0183	
TOTAL	45	0.9542		

VARIABLE Fe
BY VARIABLE GROUP

ANALYSIS OF VARIANCE

SOURCE	D.F.	SUM OF SQUARES	MEAN SQUARES	F RATIO
BETWEEN GROUPS	3	34.0646	11.3549	12.396
WITHIN GROUPS	42	38.4728	0.9160	
TOTAL	45	72.5374		

VARIABLE Al
BY VARIABLE GROUP

ANALYSIS OF VARIANCE

SOURCE	D.F.	SUM OF SQUARES	MEAN SQUARES	F RATIO
BETWEEN GROUPS	3	51.2494	17.0831	13.808
WITHIN GROUPS	42	51.96331.2372		
TOTAL	45	103.2127		

VARIABLE CEC
BY VARIABLE GROUP

ANALYSIS OF VARIANCE

SOURCE	D.F.	SUM OF SQUARES	MEAN SQUARES	F RATIO
BETWEEN GROUPS	3	592.2717	197.4239	2.311
WITHIN GROUPS	42	3588.4602	85.4395	
TOTAL	45	4180.7305		

VARIABLE KEC
BY VARIABLE GROUP

ANALYSIS OF VARIANCE

SOURCE	D.F.	SUM OF SQUARES	MEAN SQUARES	F RATIO
BETWEEN GROUPS	3	588.8038	196.8012	2.648
WITHIN GROUPS	42	3125.8504	74.4202	
TOTAL	45	3884.4538		

VARIABLE SA
BY VARIABLE GROUP

ANALYSIS OF VARIANCE

SOURCE	D.F.	SUM OF SQUARES	MEAN SQUARES	F RATIO
BETWEEN GROUPS	3	173295.3384	57765.1094	16.501
WITHIN GROUPS	42	147032.7560	3500.7800	
TOTAL	45	320328.0525		

VARIABLE TI
BY VARIABLE GROUP

ANALYSIS OF VARIANCE

SOURCE	D.F.	SUM OF SQUARES	MEAN SQUARES	F RATIO
BETWEEN GROUPS	3	0.0202	0.0067	8.039
WITHIN GROUPS	42	0.0352	0.0008	
TOTAL	45	0.0555		

VARIABLE NI
BY VARIABLE GROUP

ANALYSIS OF VARIANCE

SOURCE	D.F.	SUM OF SQUARES	MEAN SQUARES	F RATIO
BETWEEN GROUPS	3	7979.2480	2659.7493	12.204
WITHIN GROUPS	42	9153.2183	217.9337	
TOTAL	45	17132.4606		

VARIABLE SI
BY VARIABLE GROUP

ANALYSIS OF VARIANCE

SOURCE	D.F.	SUM OF SQUARES	MEAN SQUARES	F RATIO
BETWEEN GROUPS	3	136.2069	45.0690	16.100
WITHIN GROUPS	42	117.5677	2.7992	
TOTAL	45	252.7746		

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APPENDIX VI.

Analyses of Variance of the Mineralogical Composition of the Sand Fraction from the Major Soil Units.

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ANALYSIS OF VARIANCE OF SAND MINERALOGICAL DATA

VARIABLE HEAVY MINERALS
BY VARIABLE GROUP

ANALYSIS OF VARIANCE

SOURCE	D.F.	SUM OF SQUARES	MEAN SQUARES	F RATIO
BETWEEN GROUPS	3	1.7400	0.5800	0.824
WITHIN GROUPS	42	29.3697	0.6278	
TOTAL	45	29.1097		

VARIABLE K FELDSPAR
BY VARIABLE GROUP

ANALYSIS OF VARIANCE

SOURCE	D.F.	SUM OF SQUARES	MEAN SQUARES	F RATIO
BETWEEN GROUPS	3	27.6279	9.2093	8.123
WITHIN GROUPS	42	63.1654	1.5038	
TOTAL	45	90.7933		

VARIABLE NA FELDSPAR
BY VARIABLE GROUP

ANALYSIS OF VARIANCE

SOURCE	D.F.	SUM OF SQUARES	MEAN SQUARES	F RATIO
BETWEEN GROUPS	3	39.2255	13.0752	4.837
WITHIN GROUPS	42	113.5236	2.7029	
TOTAL	45	152.7491		

VARIABLE CA FELDSPAR
BY VARIABLE GROUP

ANALYSIS OF VARIANCE

SOURCE	D.F.	SUM OF SQUARES	MEAN SQUARES	F RATIO
BETWEEN GROUPS	3	45.3305	15.1102	25.704
WITHIN GROUPS	42	24.6897	0.5878	
TOTAL	45	70.0201		

VARIABLE QUARTZ
BY VARIABLE GROUP

ANALYSIS OF VARIANCE

SOURCE	D.F.	SUM OF SQUARES	MEAN SQUARES	F RATIO
BETWEEN GROUPS	3	282.9618	87.6539	12.820
WITHIN GROUPS	42	287.1637	6.8372	
TOTAL	45	550.1252		

APPENDIX VII

ANALYSIS of STANDARD SOILS and PLANT TISSUE by ICP-AES.

Abstract.

Four standard soils prepared by the Canadian Certified Materials Reference Project and one standard NBS plant tissue sample were analysed by Inductively Coupled Plasma–Atomic Emission Spectroscopy to demonstrate the applicability of this technique to the bulk elemental analysis of soil and plant materials.Accurate results for the standard soils were obtained for 16 elements while content of 19 elements determined in standard orchard leaves were within certified limits. Acceptable results for As, Cd and B in soil could not be obtained, in part due to interferences by Ti.

Introduction.

Analysis of soil materials and, to a lesser extent, plant tissue for total elemental abundance is complicated both by the wide range in compositions encountered, and by the resistance of coexisting mineral and organic materials to simple procedures of sample dissolution. In recent years a variety of analytical procedures have been used to obtain simultaneous multi-element analyses of soils including instrumental neutron activation analysis (13) and energy dispersive X-ray fluoresence (3,5). These techniques,however, require that samples and standards must be closely matched in order to compensate for matrix effects (15).

The development of inductively coupled plasma-atomic emission spectroscopy (ICP-AES) provides a technique in which matrix problems are minimalised, largely through use of the high temperature argon plasma. ICP-AES has gained some usage for:

1. geochemical analyses (2, 7, 20);
2. analysis of extractable nutrient levels from a wide range of soils (4, 9, 18);
3. bulk composition of soils (12, 14);
4. plant tissue analysis (8);
5. sediment analysis (11).

Most of these applications have, however, required either multiple sample dissolutions, or serial dilutions, to obtain accurate data for major, minor and trace element levels in the same sample (12, 16, 20).

This study was undertaken to evaluate the suitability of ICP-AES for determination of elemental abundances in plant tissue and in soil materials of varying composition using single digest solutions without serial dilutions or special sample preparation techniques.

Sample Preparation.

A description of the soils and procedures used for sample preparation are available from the Canadian Certified Reference Materials Project [4] who tabulated analytical data on these soils so that they may be used as interlaboratory standards. Sample S01 is from the C horizon of Rideau Clay, an Orthic Regosol (CSSC 1978); sample S02 is from the B horizon of a Ferro-humic Podzol developed in sandy glacial till; sample S03 is a calcareous glacial till parent material of the Guelph series, a Grey Brown

[4] Soils available from J.A. McKeague, Soil Research Institute, Central Experimental Farm, Ottawa, KIA OC6, Ontario, Canada.

Luvisol; and sample S04 is from the Ah horizon of an Orthic Black Chernozem developed in silty Lacustrine deposits. These soils have documented values for abundances of 45 elements, 18 of which are certified.

Triplicate digests of each standard soil sample were prepared using a modification of the HF–HCl dissolution method. One gram portions of each sample were ignited at 550° C, a temperature chosen to minimalise volatilisation loss of phosphorous, in porcelain crucibles. Following ignition for 8 hours samples were transferred to open Teflon beakers and treated with 20 ml concentrated HCl and 20 ml concentrated HF. The mixture is evaporated to dryness on a sand bath at 85° C, and the digestion procedure is repeated using 10 ml of each of the acids. Finally, an additional 10 ml. of HCl only is added to the residue and again evaporated to dryness to ensure complete volatilisation of the HF. The residue is then dissolved in 25 ml of 4N HCl over the sand bath, cooled, transferred to a 50 ml volumetric flask and made to volume with distilled water.

The National Bureau of Standards, Orchard Leaves, Standard Reference Material 1571 was used in this study. Triplicate digests of this Reference Material were prepared by first drying 2 gms of sample for 4 hours at 85° C in a Vycor crucible. The samples were then pre–ashed on a hot–plate with a surface temperature of 150° C for 1 hour, after which they were ignited in a muffle furnace at 550° C for 8 hours. The residue was then macerated in 10 ml 2N HCl and left to stand for half an hour before transferral to a 25 ml volumetric flask. The crucible was rinsed twice with 5 ml of 2N HCl, and the flask made to volume with 2N HCl. The carbon residue from the tissue was allowed to settle prior to analysis.

Instrumentation.

Major, minor and trace elements were determined with an ARL QA–137 direct reading spectrometer with an inductively–coupled argon plasma excitation source. The operating conditions outlined in Table 1 represent compromise conditions suggested by the manufacturer to produce acceptable results for all analysed results. Attempts were not made to optimise these conditions for any one specific element. Sample aspiration is natural with –5 cm head on the uptake capillary. This seems to minimalise the irregular sample introduction rate described on some ICP–AES instruments equipped with peristaltic pump. The torch design also allows for a comparatively low coolant flow.

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Table 1. Operating procedures for routine analysis using the ARL OA-137 instrument.

Incident Power	1850 watts
Reflected Power	<10 watts
Entrance Slit Width	12 microns
Argon Flow Rates:	
Coolant	10.5 litres per min
Sample Carrier Gas	1 litre per min.
Plasma	1.5 litres per min.
Sample Aspiration Rate	2.4 ml per min.
Observation Height	0.82 coil height
Nebuliser	Meinhart Concentric
Operating Temperature	75 C.

The instrument in this laboratory is currently equipped to analyse for 20 elements utilising the spectral lines outlined in Table II. Silicon is not determined as it is volatilised duting the soil digestion procedure,and was thus not included in the standard array for the plant tissue.

Standards and Instrumental Calibration.

Since few significant chemical interferences occur with ICP-AES, it is preferable to use pure chemical for instrumental standards. Generally 1000 ppm Atomic Absorption Standards were used for preparation of the linear curves although it was found that some commercially prepared standards were up to 20 % in error. Stock solutions for Fe and Al were prepared from 99.999 % pure chemicals. Elemental concentration ranges of sets of combined standards were chosen to bracket the elemental concentration ranges of the soil and plant digests. The elemental groupings were chosen to minimise possible interelement effects during instrument standardisation. It was found, for example, that standards from non-certified chemicals and A.A. standards made with both Ca and Mg in the same group produced results up to 12 % in error resulting from either chemical contamination or interference; a similar, though less severe, problem was observed with both Na and K in the same group. Problems also occurred in defining groups for the minor elements because some commercial A.A. standards did not describe the chemical form used in preparation.

These groups, along with spectral lines used for analysis and instrumental detection limits calculated from the standard curves produced during standardisation, are outlined in Table II. The instrument was profiled using Mn, and the interelement correlations obtained by determining spectral interference of macroelements on the minor elements were applied using the programs supplied by the manufacturer for use in the Digital PDP-1104 minicomputer which was interfaced with the ICP-AES instrument. Corrected results are printed on a DEC-writer 11 input/output terminal, and may be stored on disc for subsequent statistical analyses. Fe, Al, Ca and K were the main elements causing interference with Cu, Co,Cd, B, Pb and As.

Results.

Data in Table III illustrate a typical soil analysis result, showing analytical precision following three 15 second integrations of the analyte solutions. The variation found

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Table 2. Spectral lines, detection limits, and standard groups used for instrumental calibration.

Element	Spectral Line	Detection Limit (ppm)	Group Number	Standard Concentration Range (ppm)
Cu	2247.5	0.01195	1	0-10
Co	2286.9	0.01011	1	0-10
B	2497.7	0.00934	1	0-10
Cr	2677.2	0.00878	1	0-10
As	1937.7	0.08187	1	0-10
Pb	2203.5	0.11048	1	0-10
Cd	2265.	0.00357	1	0-10
Zn	2025.5	0.00250	2	0-100
Mn	2576.1	0.00143	2	0-100
Mo	2020.3	0.01188	2	0-100
V	3102.3	0.01283	2	0-100
Sr	2135.2	0.00090	2	0-100
P	4077.7	0.08887	2	0-100
Ca	3158.9	0.04788	3	0-1000
Na	5895.9	0.10359	3	0-1000
Mg	2790.5	0.05751	4	0-1000
K	7664.9	0.15853	4	0-1000
Fe	2599.4	0.02541	5	0-2000
Al	3082.2	0.09771	5	0-2000

Table 3. Representative soil analysis output.

Sample I.D.,SO,1

Dilution Factor, 45.1808

Element	M.V.*	Concentration**	Dil. Corr.***	R.S.D.
Cu	15.51	1.303	58.81	0.40
Co	31.48	0.848	28.28	1.80
B	73.71	1.504	67.89	3.80
Cr	40.82	3.387	152.0	0.75
As	28.24	1.087	42.82	14.85
Pb	8.24	0.388	17.9	4.11
Cd	8.77	0.088	2.97	0.51
In	124.53	2.882	129.2	0.37
Mn	1024.14	17.482	787.9	0.00
V	10.47	2.907	131.3	1.07
Sr	183.7	6.529	294.7	0.25
Mo	12.78	0.039	1.84	2.01
P	32.01	15.95	720.	0.84
Na	423.24	427.00	19281.	0.83
K	183.89	883.2	28781.	0.13
Ca	338.1	388.4	17448.	0.04
Mg	788.88	481.0	20817.	0.38
Fe	3873.23	1302.	58808.	0.04
Al	2386.81	2073.	93620.	0.47

* Mean voltage from capacitor following 3 15 sec. integrations

** Concentration in analyte solution (ppm).

***Concentration in original sample (ppm).

from the triplicate dissolutions had similar R.S.D. values as those illustrated for an individual analysis. The high R.S.D. values for Pb, As, Mo, Co and B reflect the additive effects the applied interference corrections. Table 1V presents data from up to 20 analyses per standard over a six month period during which the reference soil digests were inserted during routine analytical runs as an instrument calibration check. Such checks were run during routine analytical runs of analyses of digests of soil parent materials, clay separates and a range of soil/fly ash admixtures.

Results of analyses of the Orchard Leaves Reference Material shown in Table V were obtained during routine analyses of feed materials and forage crop tissue analysis from trials grown of sludge-amended soils.

Discussion.

The data obtained for the NBS Orchard Leaves (Table V) show lavels for all 17 certified elements are within, or very close to, those reported by NBS. These values were obtained from a series of digests over a three month period and indicate the precision of the instrument when levels of macroelements in the analyte solutions are below 200 ug gm.

Standard soil digests, however, can only be analysed with the same precision for 16 of the 19 elements on this particular instrument. Spectral interference on the As line was able to be corrected for with S04 only. Ti, present in the other soils at levels approaching 1%, was found to be partly responsible for this interference. As this element is not currently in the analytical array of this ICP-AES unit, it is impossible to apply appropriate corrections for routine analysis. At the detection limits calculated for the current calibration standards it will be possible to determine with relative precision As levels in soils to approximately 6 ug. gm as this will give analyte levels of 0.1 ug gm , using the procedure described in this article. Cadmium, present at near detection limits in all four soils, was interferred with by 5 major elements (Al, Ca, Fe, K and Mg) requiring correction factors of such magnitude that it is impossible to obtain accurate results.

Colourimetric analysis (Curcumin method) indicated that B is at prescribed level in the digests. This shows that the variable levels reported here are not caused by residual HF attack on glassware during sample preparation. The erratic levels were not found to be common with different materials during routine analyses. Fly ash samples, for

Table IV. Values and Confidence Intervals for Standard Soil Samples.

	Sample SO1		Sample SO2		Sample SO3		Sample SO4	
	Documented	I.C.P.	Documented	I.C.P.	Documented	I.C.P.	Documented	I.C.P.
	wt. %		wt. %		wt. %		wt. %	
Al	9.38 ± 0.17	9.47 ± 0.48	8.07 ± 0.18	7.49 ± 0.08	3.05 ± 0.11	2.90 ± 0.20	5.46 ± 0.15	5.95 ± 0.08
Ca	1.80 ± 0.07	1.82 ± 0.02	1.96 ± 0.10	1.95 ± 0.18	14.8*	15.0**	1.11 ± 0.06	1.22 ± 0.15
Fe	6.00 ± 0.13	5.97 ± 0.08	5.56 ± 0.16	5.60 ± 0.31	1.51 ± 0.06	1.57 ± 0.01	2.37 ± 0.07	2.63 ± 0.11
K	2.68 ± 0.08	2.54 ± 0.03	2.45 ± 0.04	2.30 ± 0.01	1.16 ± 0.05	1.11 ± 0.01	1.73 ± 0.03	1.77 ± 0.16
Mg	2.31 ± 0.10	2.15 ± 0.07	0.54 ± 0.03	0.47 ± 0.01	5.11*	4.64 ± 0.28	0.56 ± 0.04	0.56 ± 0.05
Mn	0.089 ± 0.003	0.082 ± 0.001	0.072 ± 0.002	0.068 ± 0.001	0.052 ± 0.002	0.049 ± 0.001	0.060 ± 0.002	0.058 ± 0.002
Na	1.90*	1.91 ± 0.02	1.74*	1.76 ± 0.02	0.74 ± 0.04	0.71 ± 0.01	0.97*	0.94 ± 0.01
P	0.062 ± 0.01	0.079 ± 0.001	0.30*	0.32 ± 0.01	0.046*	0.047 ± 0.001	0.090 ± 0.07	0.100 ± 0.003
	(µg/g)		(µg/g)		(µg/g)		(µg/g)	
Cr	160 ± 15	156 ± 2	16 ± 2	14 ± 0.3	26 ± 3	23 ± 1	61 ± 6	58 ± 2
Cu	61 ± 3	60 ± 2	7 ± 1	9.1 ± 0.4	17 ± 1	17 ± 1	22 ± 1	23 ± 2
Pb	21 ± 4	26 ± 6	21 ± 4	27 ± 6	14 ± 3	19 ± 3	16 ± 3	15 ± 3
Sr	-	327 ± 15	340 ± 50	344 ± 19	217 ± 29	213 ± 14	170 ± 18	180 ± 9
V	139 ± 8	138 ± 2	64 ± 10	68 ± 2	44*	39 ± 2	90 ± 11	90 ± 2
Zn	146 ± 5	130 ± 2	124 ± 5	116 ± 3	52 ± 3	46 ± 1	94 ± 3	91 ± 3
As*	1.9	27 ± 4	1.2	21 ± 3	2.6	13 ± 2	7.1	10 ± 3
B *	20	163 ± 87	2.7	93 ± 35	22	180 ± 140	43	201 ± 160
Cd*	0.15	7.8 ± 0.1	0.18	7.4 ± 0.1	0.14	2.5 ± 0.1	0.42	3.9 ± 0.1
Co*	33	37 ± 3	13	16 ± 5	12	10 ± 2	15	16 ± 1
Mo*	2	2 ± 1	2	2 ± 1	2	1.3 ± 0.8	1	1.4 ± 0.5

* levels not certified

** sample diluted for analysis

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Table 6. Elemental content of NBS standard reference material 1571.

Element	NBS Reported value*	ICP value
Cu	12 ± 1	10.8 ± 0.3
Co	(0.2)	0.4 ± 0.1
B	33 ± 3	34.8 ± 0.8
Cr	2.8 ± 0.3	3.00 ±0.08
As	10 ± 2	8.8 ± 0.2
Pb	48 ± 3	42.0 ± 1.0
Cd	0.11 ± 0.01	0.13 ± 0.03
Zn	28 ± 3	22.0 ± 0.3
Mn	81 ± 4	78.8 ± 0.8
V	n.a.	0.88 ± 0.21
Sr	37 ± 1	38.3 ± 0.8
Mo	0.3 ± 0.1	0.19 ± 0.09
Ba	82 ± 8	78.8 ± 0.8
Fe	300 ± 30	240 ± 1
Al	n.a.	234 ± 8
P	0.21 ± 0.01 %	0.19 ± 0.01
K	1.47 ± 0.03 %	1.40 ± 0.040
Ca	2.08 ± 0.03 %	2.03 ± 0.01
Mg	0.82 ± 0.02 %	0.88 ± 0.01

* All values in ppm except where indicated.

example, have given excellent replication for B analyses. Clay separates, analysed both following routine sample digestion and by direct suspension aspiration (Appendix VIII), also produced analyses whch were highly consistent at B concentrations as high as 300 ug gm^{-1} The memory effects described by other analysts were observed during this study (10). Sample analysis for S01, S03 and S04 following instrument calibration repeatedly gave levels between 30 – 50 ug. gm , but subsequent analyses following the routine wash period (45 seconds) produced steadily increasing levels to as high as 300 ug gm although this level would revert to that certified if the nebuliser was flushed with 2N HCl for several minutes prior to analysis. The above discussion indicates that B must be undergoing surface absorption or adsorption to the fused quartz within the plasma region.

As the photomultipliers record emission from the plasma region only, the B absorption is most likely to be on the upper periphary of the inner quartz tube of the torch. Boron is possibly forming a covalent bond which is not stable at the high temperatures present at the base of the plasma, thus explaining the decrease in B levels following a long wash interval. This transitional bonding would, however, provide a source for the increasing number of B photons reaching the photomultiplier, thus producing an apparent high level in the analyte solution.

These problems are most apparent in the samples relatively high in P, which suggests that some element present in P– bearing minerals may be responsible for formation of borate complexes. The fact that manufacturers of the new HF resistant nebuliser for this instrument advise that with HF levels above 6 % in the analyte solution B analyses will give R.S.D's as high as 50 % indicates that F may be involved in this complexation. Fluorine, found in P– bearing minerals such as fluorapatite, and present in the CCRMP standard soils at up to 700 ug. gm^{-1} may thus be responsible indirectly for the poor analytical performance with B.

Conclusion.

ICP–AES has proven an efficient method for bulk analysis of soil and plant tissue digests of varying compositions. The addition of more channels, especially Ti, may allow problems in As determination to be overcome. Analysis for Cd, because of inherently low levels in soils compared to those of macroelements , is not feasible without

additional sample preparation such as solvent extraction. Boron analysis, on the other hand, will continue to be unreliable because instrumental problems appear, at present, to be insolvable.

The main advantages of ICP-AES are the speed and simplicity of operation producing data of high accuracy and reproducibility with analyte solutions of up to 15 % dissolved salts and with elemental concentration ranges in excess of 3 orders of magnitude. It is possible to correct for most spectra; interferences which occur in solutions containing 1 - 2000 ug gm^{-1} of the major elements. These interferences are almost non existent in solutions where maximum concentrations of these elements are below the 200 ppm. level. In this laboratory, a trained operator can analyse 20 - 25 samples per hour, allowing time for instrument restandardisation, for up to 19 elements using only one digestion with no serial dilutions for soils and plant tissues.

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APPENDIX VIII

ANALYSIS of SOIL CLAY SEPARATES by ICP-AES with SUSPENSION ASPIRATION.

Abstract.

Samples of clay separates (<0.2, 0.2 – 2 and < 2 microns) were analysed by ICP–AES following routine dissolution procedures. Suspensions (0.2 %) of these separates were then analysed to determine whether accurate compositional data could be obtained. Once correction for the decrease in aspiration rate because of suspension viscosity had been made, accurate analyses were produced for the following elements: Al, Ca, Fe, K, Mg, Na, B, Cr, Zn, Mn, V, Sr, and P. Clay mineral standards were then used for instrumental calibration, and analyses of the separates against these standards produced data of high accuracy for numerical studies, with the added advantage of producing producing estimates of Si content. Advantages of this method are elimination of sample preparation procedures, relative speed of analysis and simultaneous multielement capability.

Introduction.

Inductively-coupled plasma is a relatively new excitation source in emission spectrometry (Boumans, 1978). Plasmas, by definition, are gases in which a significant fraction of the atoms or molecules is ionized (Fassel and Knisely, 1974). The basic research work of the inductively-coupled plasmas into an analytical system has been well documented (Fassel and Knisely, 1974; Boumans and de Boer, 1975; Boumans, 1978; Fassel, 1978).

In the ARL-QA137 instrument in this laboratory the analyte solution is aspirated into a Meinhart Concentric nebuliser where the flow of argon gas converts a proportion of the solution into an aerosol which is then sprayed into the centre of an argon plasma. The inductively-coupled argon plasma is a stream of argon atoms which are inductively heated by a radio-frequency coil (1.65 KW). This heating of the argon passing through the radio-frequency field strips electrons from the argon atoms to produce a plasma of argon ions with an operating temperature in the centre of 6000-10000° K; the plasma is ignited by a Tesla spark.

Thus the analyte solution is introduced into a very high temperature zone. Elements in this solution thus emit their characteristic radiation, and this is focused into a conventional air path spectrometer. The spectral lines are diffracted from the main grating and detected by fixed photomultipliers mounted along the Rowland circle of the spectrometer.

In the Earth Sciences ICP-AES has been used for geochemical analyses (Bouman 1977; Floyd *et al*, 1980; Odegrad, 1981; Walsh and Howrie, 1980), for determination of bulk composition of soils and sediments (Larson *et al*, 1979; McQuacker *et al*, 1979), and from a wide range of soils (Dalquist and Knoll, 1978; Jones, 1977; Soltanpour *et al*, 1979). All these applications have, however, required that samples be converted to solution form prior to analysis.

Boumans (1978) indicated that ICP-AES, although primarily suited for analysis of liquid samples, can directly handle solids. Thus this study was undertaken to determine whether ICP-AES could provide an accurate analysis of dilute clay suspensions without prior dissolution. A secondary objective was to determine whether suspensions of

standard A.P.I. reference clay minerals, subsamples of which had been previously analysed by electron microprobe (Smith and Cavell, 1978), could be used as standards for routine analysis to minimise matrix effects apparent in the first phase of this study.

MATERIALS and METHODS.

Sample Preparation Techniques.

Samples were taken from soil parent materials and from pedons representing major soil series in North Eastern Alberta. 100 gram subsamples were dispersed in distilled water for three minutes by ultrasonification at 400 W using a probe-type vibrator (Edwards and Bremner, 1967). Total clays (< 2 microns),medium and coarse clays (2 - 0.2 microns) and fine clays (< 0.2 microns) were separated from the resulting suspensions by a combination of gravity separation and centrifugation as outlined in McKeague (1978). The separates were flocculated using 1 M $CaCl_2$ solution, washed of excess electrolyte with distilled water and freeze dried for storage prior to subsequent analysis. C.E.C. was determined by measuring the Ca^{++} displaced by NaOAc using atomic absorption spectrometry.

Duplicate digests of the Ca-saturated clay separates were prepared by dissolution with HF-HCl as described by Pawluk (1967), with 2.0 grams of sample being dissolved in a final solution of 50 ml.

Preliminary experiments indicated that suspensions at the same concentrations as used for the digests gave a 25 % or more decrease in aspiration rate and thus in analytical results. Compromise conditions using suspensions containing between 0.1 - 0.2 grams of Ca^{++} and NH_4^+ saturated clay in distilled water produced optimal results,while maintaining levels of minor elements above instrumental detection limits.

Samples of API reference clay minerals,which had been previously analysed by electron microprobe (Smith and Cavell ,1978), were obtained for use as instrumental calibration standards. These were prepared as 0.2 % suspensions and used to generate standard curves for six macroelements (Si,Fe, Al, Ca, Mg, K). Data obtained using the clays as reference standards are on a water-free basis (Smith and Cavell,1978), and those obtained by dissolution are based on sample weight at 105° C.

Instrumentation.

Major and minor elements were determined with an ARL QA-137 direct reading spectrometer with an inductively- coupled argon plasma excitation source.The operating conditions outlined in Table I represent compromise conditions suggested by the manufacturer to produce acceptable results for all analysed elements. Attempts were not made to optimise these conditions for any one element. Sample aspiration is natural with a -5 cm head on the uptake capillary. The torch design also allows for a comparatively low coolant flow. The most critical parameter as far as analytical precision is concerned is carrier gas flow rate (Boumans, 1978). Thus any variation in solution aspiration rate into this carrier gas will introduce error into the analysis because it will affect the number of molecules entering the plasma for dissociation into atoms or ions which are, in turn, excited by the plasma energy to emit their characteristic spectral radiation.

The instrument in this laboratory is currently equipped to analyse for 20 elements utilising the spectral lines outlined in Table II. Only 14 of these elements were analysed for in this study.

Standards and Instrument Calibration.

Since few significant chemical interferences occur with ICP-AES, it is preferable to use pure chemical for instrumental standards. Elemental concentration ranges of sets of combined standards were chosen to bracket the elemental concentration ranges expected for the clay digests and suspensions. The elemental groupings were chosen to minimise possible interelement effects during instrument standardisation. These groups, along with spectral lines used for analysis and instrumental detection limits calculated from the standard curves produced during standardisation,are outlined in Table II. The instrument was profiled using Mn.

The data processing analytical package supplied by ARL for use with the PDP 1104 minicomputer which is interfaced with.the ICP-AES instrument was used at all stages of this study.The results were printed on a DEC-writer II input-output terminal,and were also stored on disc for subsequent statistical analysis.

RESULTS and DISCUSSION.

Figure I shows comparisons between the analytical results obtained from both digests and suspensions of the clay separates by ICP-AES.

FINE PRINT

Table 1. Operating procedures for routine analysis using the ARL 6A-137 instrument.

Incident Power	1850 watts
Reflected Power	<10 watts
Entrance Slit Width	12 microns
Argon Flow Rates:	
Coolant	10.5 litres per min
Sample Carrier Gas	1 litre per min.
Plasma	1.5 litres per min.
Sample Aspiration Rate	2.4 ml per min.
Observation Height	0.83 coil height
Nebuliser	Meinhart Concentric
Operating Temperature	75 C.

FINE PRINT

Table II. Spectral lines, detection limits, and standard groups used for instrumental calibration.

Element	Spectral Line	Detection Limit (ppm)	Group Number	Standard Concentration Range (ppm)
Cu	3247.5	0.01185	1	0-10
Co	3388.8	0.01011	1	0-10
B	2497.7	0.00834	1	0-10
Cr	3877.2	0.00976	1	0-10
As	1937.7	0.08167	1	0-10
Pb	2203.5	0.11048	1	0-10
Cd	2265.	0.00357	1	0-10
Zn	2025.5	0.00250	2	0-100
Mn	2576.1	0.00143	2	0-100
Mo	2020.3	0.01186	2	0-100
V	3102.3	0.01253	2	0-100
Sr	2136.2	0.00080	2	0-100
P	4077.7	0.08837	2	0-100
Ca	3158.9	0.04789	3	0-1000
Na	5895.9	0.10389	3	0-1000
Mg	2790.8	0.08781	4	0-1000
K	7664.9	0.18853	4	0-1000
Fe	2599.4	0.02841	5	0-2000
Al	3082.2	0.08771	5	0-2000

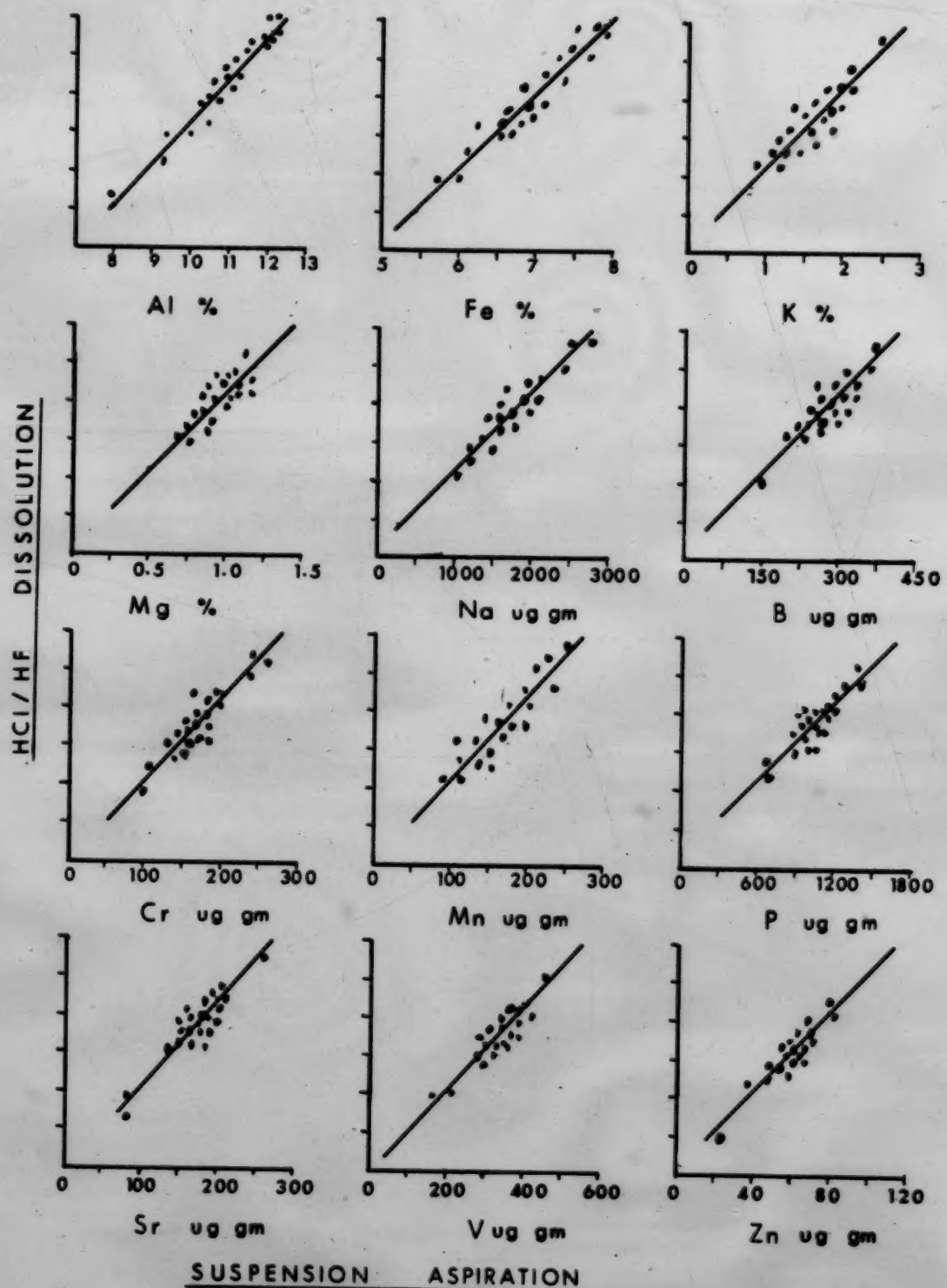

Figure I. Comparative plots for Al, Fe, K, Mg, Na, B, Cr, Mn, P, Sr, V and Zn contents in clay separates.

The high coefficients of determination (r^2) demonstrate clearly the potential of suspension aspiration for rapid and accurate analysis of the bulk chemistry of clay separates. The b values (slopes) were not significantly different for any of the 13 elements determined, all being between 1.07 and 1.09. The increased viscosity of the clay suspensions induces an aspiration rate approximately 8% slower than that of digest and standard solutions. This aspiration rate decrease is thus directly responsible for the analytical variation observed, amd may thus be corrected by use of a factor (1.08).

Five A.P.I. reference clay minerals, for which microprobe analyses of macroelement content were available, were used to create clay suspension standards which should not show the viscosity differences obtained with chemical standards. Suspensions of these clays at concentrations of between 0.01 and 0.25 % were then analysed to determine the utility of the standard curves for analysis of unknown soil clay separates (Table IV). Analyses of the soil clay suspensions produced data which were from 8 – 12 % higher than those obtained by solution analyses. The values for the clay standards are calculated on a water-free basis (Smith and Cavell, 1978), and the 8 – 12 % variation compares favourably with amounts of absorbed and interlayer water expected in such mixed clays from D.T.A. and T.G.A. data (Grim, 1968).

C.E.C. data obtained from difference between Ca values of Ca^{++} and NH_4^+ saturated suspensions are compared with those obtained by A.A.S. in Table IV.The close agreement between the independent analyses indicates the precision of analysis of these clay separates by suspension aspiration using ICP-AES. A major advantage in using these clay standards is the ability to obtain an accurate analysis for Si, which is volatilised during the routine digestion procedures.

CONCLUSIONS.

ICP-AES has been shown to be capable of thermally decomposing crystalline clay materials to provide accurate and reproducible analyses of bulk composition. Furthermore, matrix effects resulting from visiosity differences between chemical standards can be minimised by using standard reference clay material suspensions as calibration standards for the instrument. The availibility of clay minerals with certified chemical analyses would increase the application of this method of analysis in studies of clay mineral compositional changes resulting from weathering or diagenetic processes.

FINE PRINT

Table III. Analysis of A.P.I. standard Nontronite illustrating agreement between suspension analyses at varying concentrations and that documented by Electron Microprobe analysis.

Element	Electron Microprobe	ICP-AES *
Si	24.571 #	24.674 ± 0.005
Al	3.865	3.742 ± 0.006
K	0.00	100 ± 4 ppm
Mg	0.398	0.381 ± 0.003
Ca	1.358	1.365 ± 0.004
Fe	26.153	26.217 ± 0.002

Data in %

* Mean based on 10 analyses at concentrations between 0·15 and 0·75 %.

FINE PRINT

Table VI. Comparison of CEC data for clay separates using AAS and suspension analyses by ICP-AES.

Sample	AAS.	ICP-AES
Bulk clay	48.2	46.9
Fine clay	74.7	76.2
Coarse clay	35.5	33.6
Bulk clay	40.9	41.8
Bulk clay	32.1	30.6
Fine clay	77.1	76.8

* Data in me. per 100 gm clay.

This technique means it would be possible to take an unknown clay suspension, gravimetrically determine the concentration, and analyse by ICP-AES following dilution of a subsample to the required concentration. Separate aliquots of the same suspension could be saturated with different cations and used for X.R.D. and/or C.E.C. analyses.

For routine analyses of composition of clay separates , the main advantages of this technique are its simplicity, speed and accuracy. An operator can analyse 20 -25 samples per hour for a wide range of elements with no tedious sample digestion being required.

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